Application Note

EMPOWERING RESULTS
Elemental Analysis | GC Mass Spectrometry | Metallography

Instrument: Pegasus® BTX and Pegasus HRT+

Battery Solvent Characterization: Identifying Impurities in Dimethyl Carbonate

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Key Words: Battery Electrolyte, Solvent Impurities, Oxygenates

Introduction

Dimethyl carbonate (DMC) is known as an environmentally friendly solvent used in many product streams, including development of rigid plastics, oxygenated additives for diesel, and EPA-approved VOC-exempt coatings and paints. Determination of impurities in DMC is crucial to prove suitability for use and prevent side-reactions in high-performance material production, especially when used as battery electrolyte solvent. The presence of unexpected organic species in DMC can reduce the overall efficiency of the batteries by degrading solid electrolyte interfaces on battery anodes, creating complexes that consume lithium ions, or producing unexpected gas buildup that leads to safety hazards during battery use. A clearer understanding of unintentional byproducts in DMC assists with refining the solvent production process, improving energy efficiency for generating high-purity solvent and for downstream solutions dependent on quality components.

The extraordinary sensitivity of the *Pegasus* BTX allows for detection of below-ppb-level contaminants. Coupled with complementary data from the high-resolution *Pegasus* HRT+, confident identification of byproduct species including nitriles, alcohols, and other hydrocarbons can be confirmed.

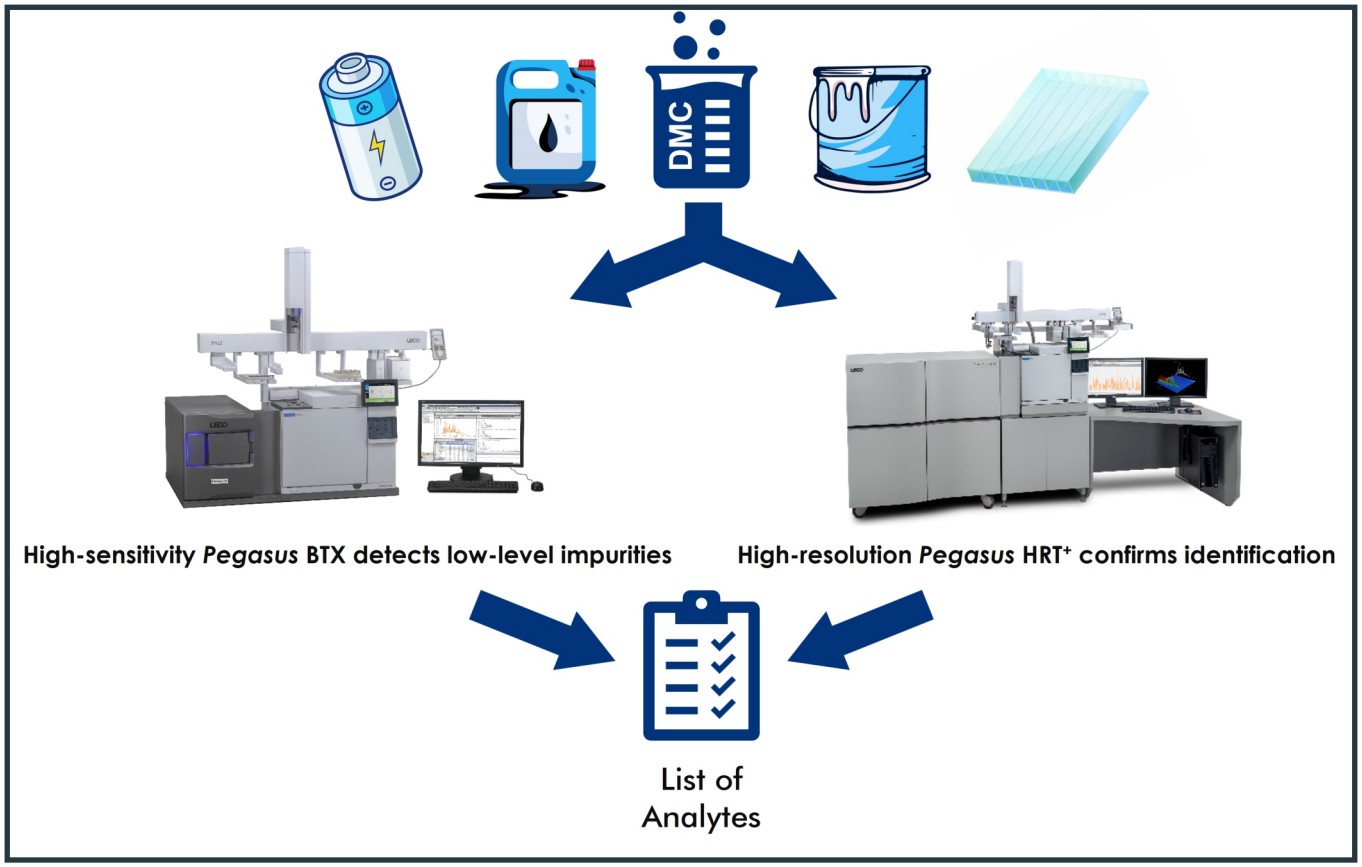


Figure 1. Workflow for identification of analytes of interest in dimethyl carbonate solvent using Pegasus BTX and Pegasus HRT+.

Experimental

A producer-provided sample of dimethyl carbonate solvent was analyzed on the *Pegasus* BTX and *Pegasus* HRT$^+$ to assess purity and identify potential unknown contaminants. After a short gas chromatography (GC) separation, electron ionization (EI) mass spectral information was produced on the *Pegasus* BTX, while the *Pegasus* HRT$^+$ produced high-resolution, accurate mass spectra in multiple modes, including EI and methane-assisted positive chemical ionization (PCI) using a single ionization source. EI spectra for peaks of interest were library-matched against NIST and Wiley spectral libraries for preliminary identification. High resolution accurate mass was leveraged to further confirm library hit assignments; in cases where molecular ion was low abundance or not present in EI spectra, PCI spectra from corresponding peaks were used to confirm molecular ion and other methane-adducts when available.

Table 1: Acquisition Parameters for Solvent Analysis.

Gas Chromatograph	**Agilent 8890 GC**		
Injection	1 µL liquid injection, split (20:1 in EI mode, 5:1 in PCI mode) @ 250 °C		
Carrier Gas	He @ 1.0 mL/min, constant flow		
Column	Rt-QBond, 15 m x 0.25 mm i.d. x 8.00 µm coating		
Temperature Program	75 °C ramped 25 °C/min to 250 °C, hold for 5 min		
Transfer Line	300 °C		
Mass Spectrometer	**LECO *Pegasus* BTX**	**LECO *Pegasus* HRT$^+$ EI**	**LECO *Pegasus* HRT$^+$ PCI**
Ion Source Temperature	250 °C	250 °C	165 °C
Electron Energy (eV)	70	70	140
Mass Range	10-800 m/z	10-800 m/z	60-1000 m/z
Acquisition Rate	10 spectra/s	10 spectra/s	10 spectra/s
CI Gas	--	--	Methane

Results and Discussion

Several major impurities, mostly oxygenated reaction byproducts, were identified using EI similarity scores on both the HRT$^+$ and BTX, as can be seen in the labeled, filtered analytical ion chromatogram (AIC) traces and table below.

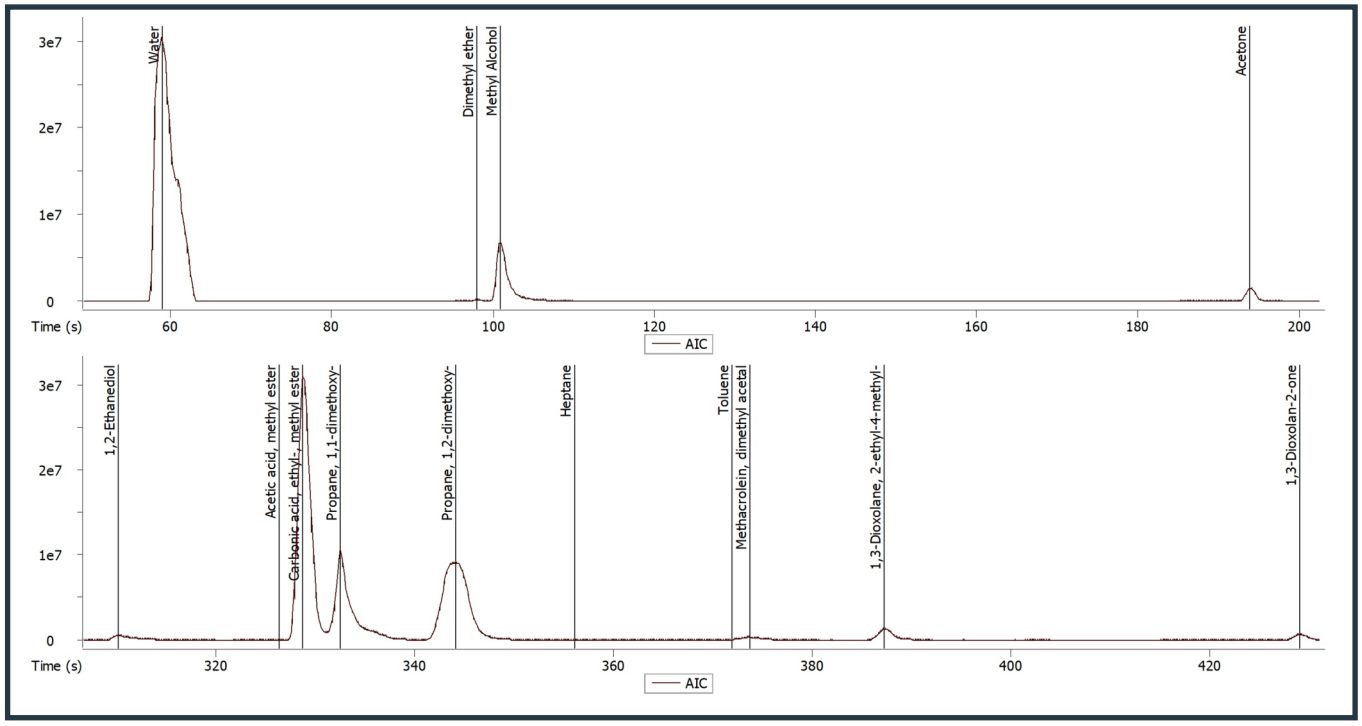
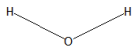
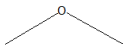
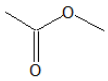
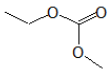
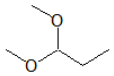
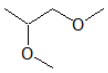
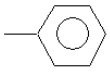


Figure 2. Pegasus HRT$^+$ EI AIC Chromatogram zoomed to analytes of interest eluting before (top) and after (bottom) DMC solvent peak.

Table 2: Major impurities identified by complementary Pegasus HRT$^+$ and Pegasus BTX analyses showing analyte structure, name, library match similarity scores, retention times for EI spectra, and PCI species used to confirm molecular formula.

Structure	Name	Chemical Formula	CAS	HRT$^+$ EI Similarity Score (/1000)	HRT$^+$ EI RT (s)	HRT$^+$ CI Species Present	BTX RT (s)	BTX Similarity Score (/1000)
	Water	H_2O	7732-18-5	967	59.0	n/a	56.5	970
	Dimethyl Ether	C_2H_6O	115-10-6	881	98.0	n/a	95.5	924
	Methanol	CH_4O	67-56-1	965	100.9	n/a	97.5	930
	Acetone	C_3H_6O	67-64-1	946	193.9	n/a	187.3	918
	1,2-Ethanediol	$C_2H_6O_2$	107-21-1	927	310.2	$[M+H]^+$	306.5	910
	Methyl Acetate	$C_3H_6O_2$	79-20-9	635	326.4	n/a	202.6	917
	Ethyl methyl carbonate	$C_4H_8O_3$	623-53-0	875	328.8	$[M+H]^+$	324.7	821
	1,1 Dimethoxy propane	$C_5H_{12}O_2$	4744-10-9	799	332.6	n/a	332.1	910
	1,2 Dimethoxy propane	$C_5H_{12}O_2$	7778-85-0	927	344.2	$[M-H]^+$	338.4/ 340.6	891/ 892
	Heptane	C_7H_{16}	142-82-5	905	356.1	n/a	347.6	890
	Toluene	C_7H_8	108-88-3	592	372.0	$[M+H]^+$	368.0	633
	Methacrolein, dimethyl acetal	$C_6H_{12}O_2$	23230-91-3	834	373.7	M^+	369.7	833
	2-Ethyl-4-methyl-1,3-dioxolane	$C_6H_{12}O_2$	4359-46-0	898	387.3	$[M+H]^+$	383.3	926
	Cyclic ethylene carbonate (1,3-dioxolan-2-one)	$C_3H_4O_3$	96-49-1	901	429.0	$[M+H]^+$	424.8	832

Additional confirmation for some analytes was achieved by confirming molecular formula using either the M^+ from EI or $[M+H]^+$ species from the PCI spectra of peaks that had retention times corresponding to the tentatively identified EI peak. One example is the confirmation of 1,2-ethanediol, shown below.

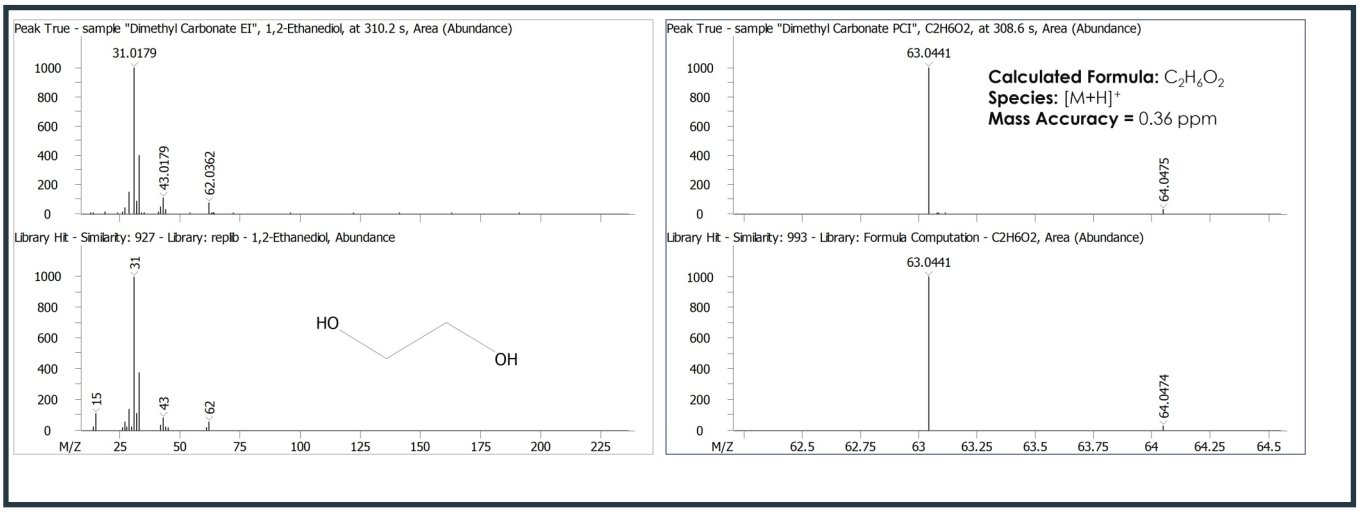


Figure 3. High-resolution Peak True (Deconvoluted) and Library-matched EI spectra (left) of 1,2-ethanediol from Pegasus HRT⁺ with corresponding PCI spectra zoomed in to $[M+H]^+$ with match to calculated spectra generated using automated formula computation.

The high mass accuracy of other major fragments in PCI spectra can also contribute to higher confidence in molecular formula assignment, as seen in the example of 2-ethyl-4-methyl-1,3-dioxolane in Figure 4 and Table 3.

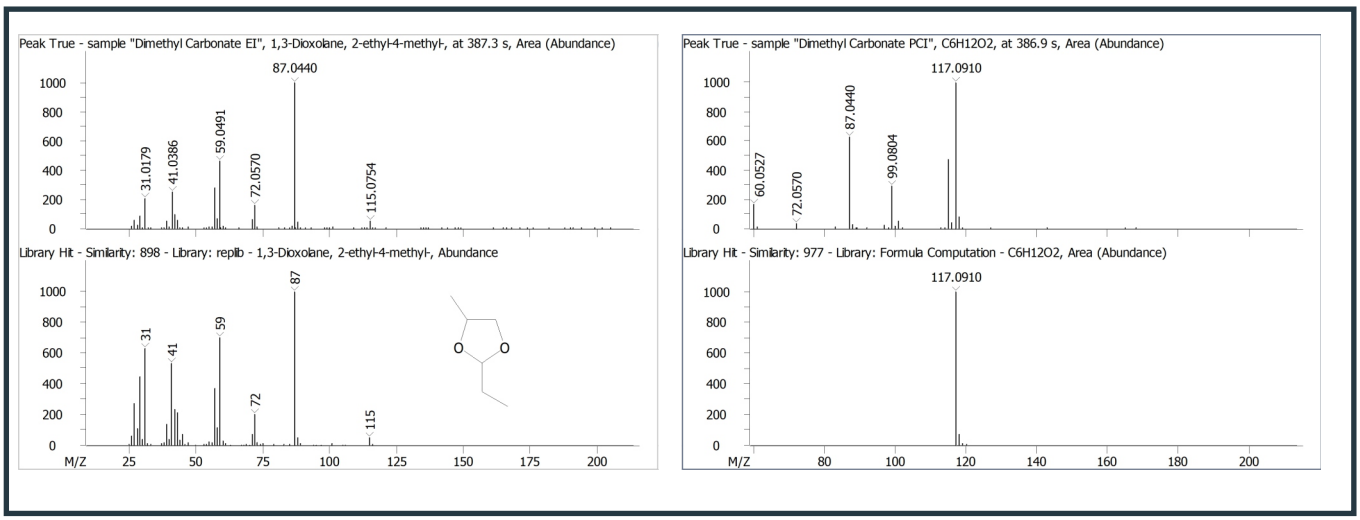


Figure 4. High-resolution Peak True (Deconvoluted) and Library-matched EI spectra (left) of 2-ethyl-4-methyl-1,3-dioxolane from Pegasus HRT⁺ with corresponding PCI spectra (right) showing structurally significant fragments in addition to $[M+H]^+$ with match to calculated spectra generated using automated formula computation.

Table 3: Masses from PCI Peak True (Deconvoluted) Spectrum of 2-ethyl-4-methyl-1,3-dioxolane with calculated formula and mass accuracies.

Observed Mass	Formula	Mass Accuracy (ppm)	Abundance	Species
117.0910	$C_6H_{13}O_2$	0.02	1000	$[M+H]^+$
115.0754	$C_6H_{11}O_2$	0.04	473	fragment
99.0804	$C_6H_{11}O$	-0.01	288	fragment
87.0440	$C_4H_7O_2$	-0.58	628	fragment

In another case with the analyte ethyl-methyl-carbonate, in addition to a major fragment, there were also common methane-assisted CI adducts $[M+C_3H_5]^+$ and $[M+C_2H_5]^+$ present in the PCI spectra to further enhance confidence in the EI library hit assignment that did not have a molecular ion present.

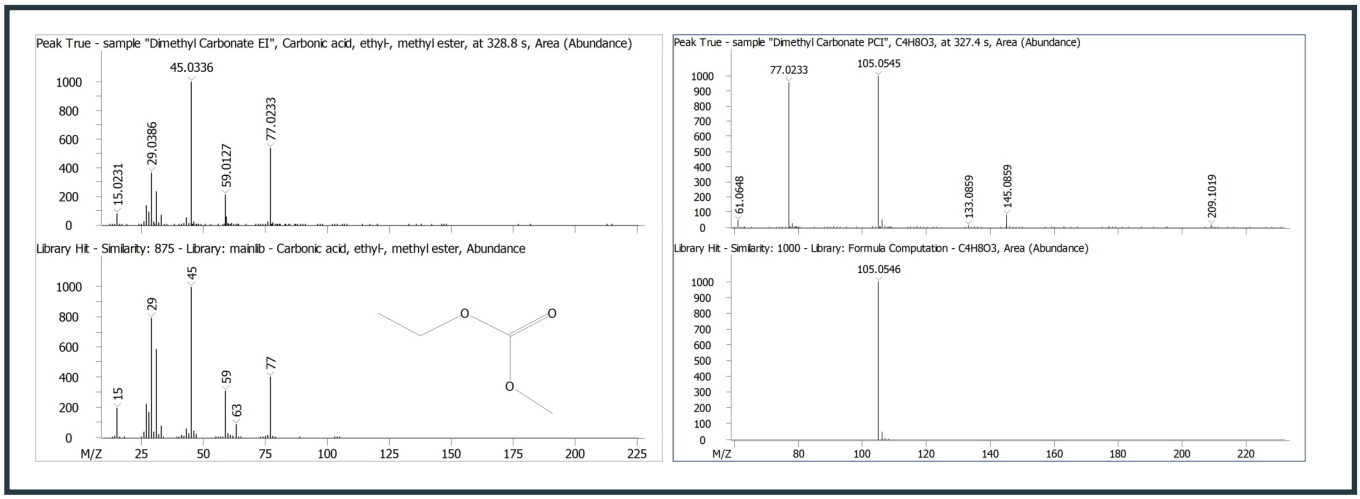


Figure 5. High-resolution Peak True (Deconvoluted) and Library-matched EI spectra (left) of ethyl-methyl-carbonate from Pegasus HRT⁺ with corresponding PCI spectra (right) showing common methane-assisted CI adducts in addition to $[M+H]^+$ with match to calculated spectra generated using automated formula computation.

Table 4: Masses from PCI Peak True (deconvoluted) spectrum of ethyl-methyl-carbonate with calculated formula and mass accuracies, including common methane-assisted CI adducts.

Observed Mass	Formula	Mass Accuracy (ppm)	Abundance	Species
145.0859	$C_7H_{13}O_3$	-0.41	83	$[M+C_3H_5]^+$
133.0859	$C_6H_{13}O_3$	-0.01	13	$[M+C_2H_5]^+$
105.0545	$C_4H_9O_3$	-0.97	1000	$[M+H]^+$
77.0233	$C_2H_5O_3$	0.22	955	fragment

Isomers of dimethoxypropane were also expected to be present in the DMC sample, but several deconvoluted peaks were present that had similarity matches greater than 800/1000 to the same library spectra. Without true retention-time-matched standards to confirm, only tentative identifications could be made for a few of these peaks. However, the power of deconvolution can be seen in the way the proper masses are attributed to each Peak True spectrum from the *Pegasus* BTX, especially in the case of the co-eluting ethyl-methyl-carbonate peak where the quantitation mass signal would otherwise be entirely buried under the tail of one of the putative 1,1-dimethoxypropane peaks.

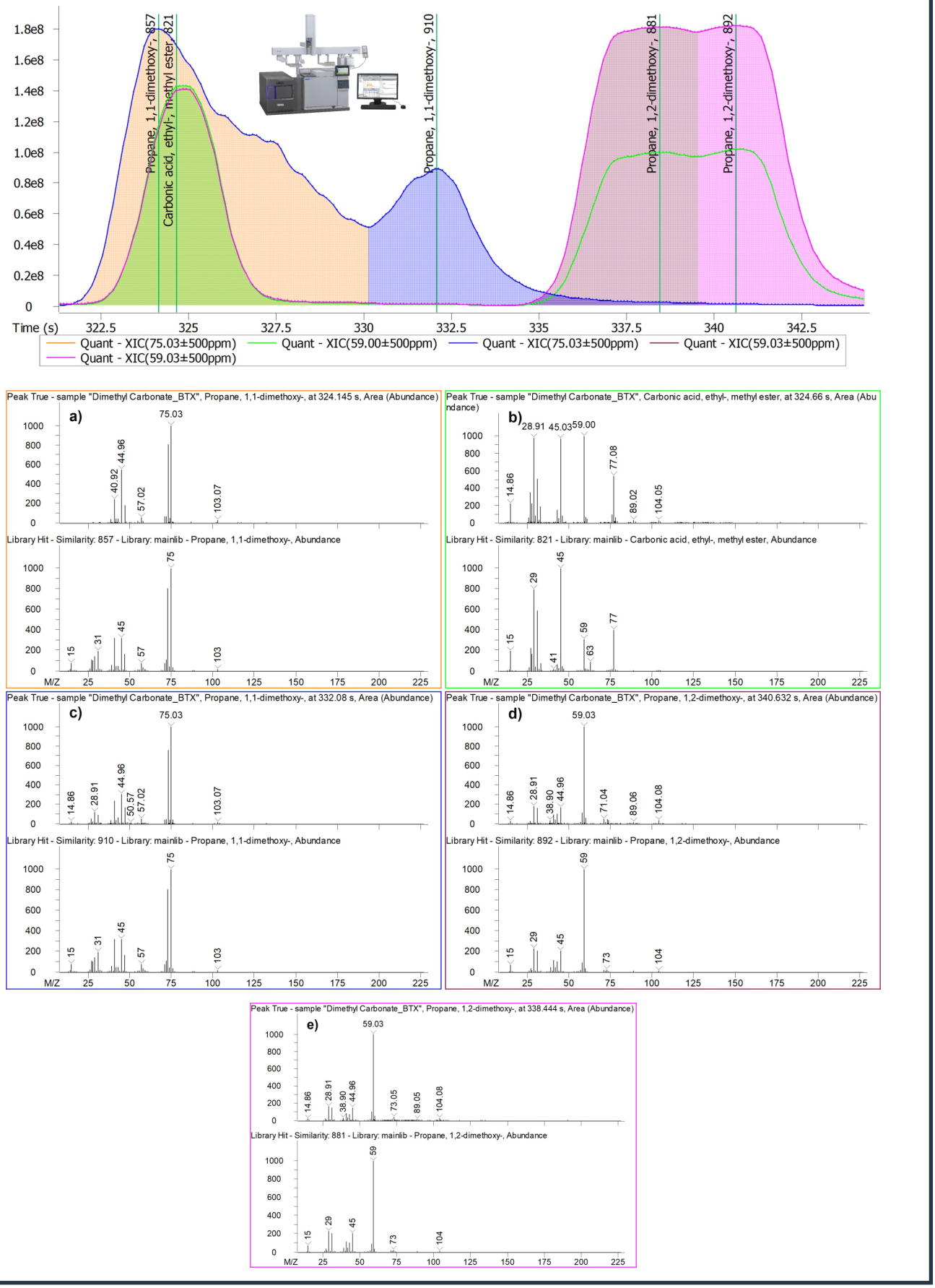


Figure 6. Chromatogram from Pegasus BTX DMC analysis zoomed in to elution region for dimethoxypropane isomers shown with overlaid quantitation masses from a variety of detected peaks, labeled with putative library matches and similarity scores (top). Peak True spectrum with corresponding matched library hit spectrum are shown below in order of elution (a-e).

While the high-resolution mass spectral information provides the greatest confidence in formula assignment, the exceptional sensitivity of the *Pegasus* BTX system was able to detect many more peaks of potential interest, including additional oxygenated species as well as several nitriles and functionalized benzene rings. A list of additional analytes identified using the *Pegasus* BTX with library similarity scores greater than 800/1000 can be seen in the labeled chromatogram and Appendix 1.

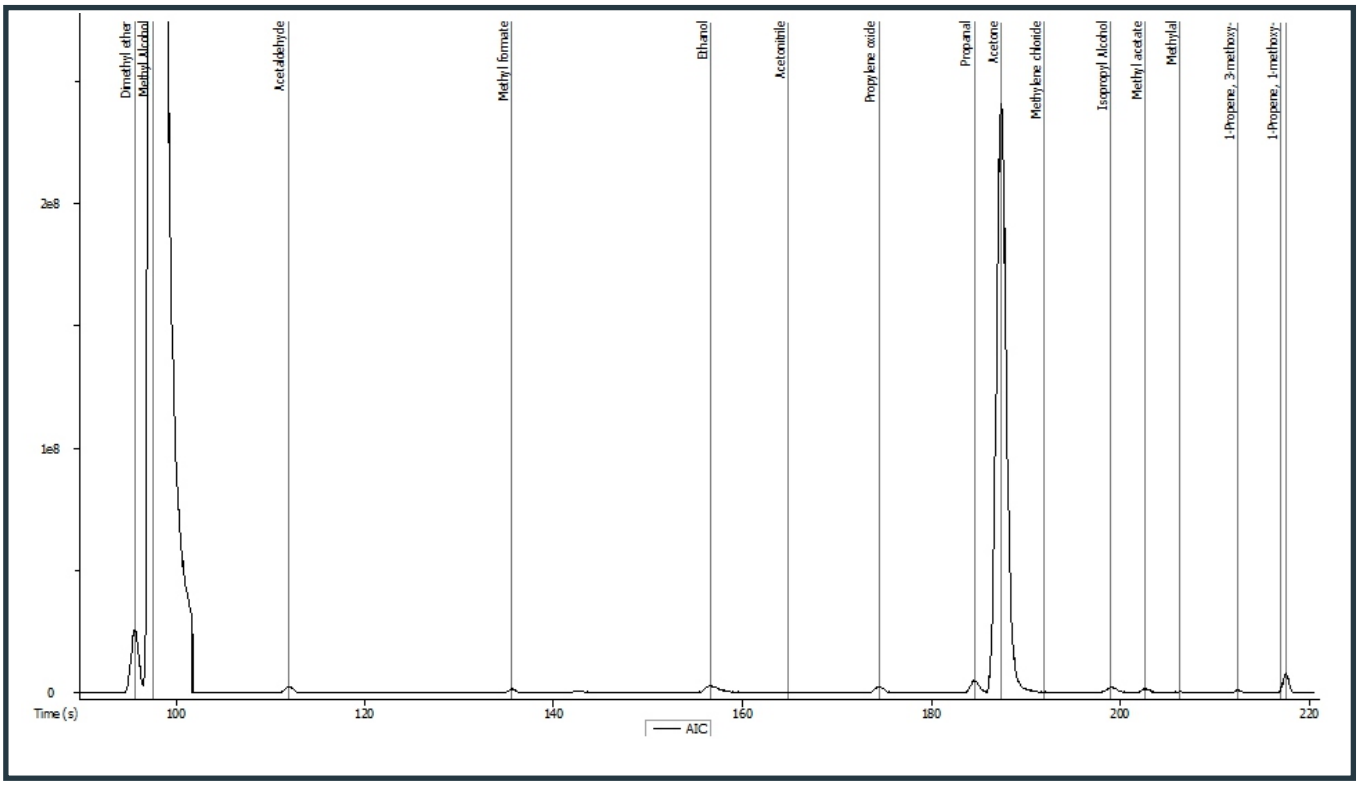


Figure 7. AIC Chromatogram from Pegasus BTX analysis of DMC zoomed in close to baseline in elution region before DMC solvent peak. Many previously undetected low concentration analytes are identified with excellent library similarity scores.

Conclusion

Unparalleled sensitivity of the *Pegasus* BTX paired with high-resolution mass spectral data from the *Pegasus* HRT$^+$ confirmed identification of several previously undetected compounds of interest in a sample of dimethyl carbonate, providing useful insight into the solvent manufacturing process.

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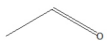
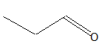
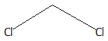
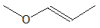
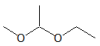
Appendix 1: Additional low-level analytes of interest detected and identified with the enhanced sensitivity provided by the *Pegasus* BTX.

Structure	Name	Chemical Formula	CAS	BTX RT (s)	Similarity Score (/1000)
	Acetaldehyde	C_2H_4O	75-07-0	111.9	912
	2-Butene	C_4H_8	590-18-1	142.5	888
	Ethanol	C_2H_6O	64-17-5	156.5	923
	Acetonitrile	C_2H_3N	75-05-8	164.7	959
	Propylene oxide	C_3H_6O	75-56-9	174.4	929
	Propanal	C_3H_6O	123-38-6	184.5	910
	Methylene chloride	CH_2Cl_2	75-09-2	191.9	911
	Isopropyl Alcohol	C_3H_8O	67-63-0	198.9	851
	Methylal	$C_3H_8O_2$	109-87-5	206.3	705
	1-Propene, 3-methoxy-	C_4H_8O	627-40-7	212.4	868
	1-Propene, 1-methoxy-	C_4H_8O	7319-16-6	216.9	805
	Propanenitrile	C_3H_5N	107-12-0	217.5	888
	Ethane, 1-ethoxy-1-methoxy-	$C_5H_{12}O_2$	10471-14-4	314.4	901
	Methyl methacrylate	$C_5H_8O_2$	80-62-6	329.6	833
	Benzene, 4-ethenyl-1,2-dimethyl-	$C_{10}H_{12}$	27831-13-6	335.1	866
	Benzene, 1-ethenyl-4-ethyl-	$C_{10}H_{12}$	3454-07-7	365.1	799
	2,4-Dimethylstyrene	$C_{10}H_{12}$	2234-20-0	447.2	814
	Benzene, 1-ethenyl-3-ethyl-	$C_{10}H_{12}$	7525-62-4	455.5	814
	Decanal	$C_{10}H_{20}O$	112-31-2	505.3	879