Supporting Information for:

Rapid Detection of Bacterial Endotoxins in Ophthalmic Viscosurgical Device Materials by Direct Analysis in Real Time Mass Spectrometry

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Agilent 6540B accurate mass Q-TOF operating parameters

DART source was operated at the same condition as with the LTQ MS. QTOF operating parameters are as follows; Neg mode→Gas temperature set to 200^{o}C, with 8.5 L/ min flow, Vcap-1000V, fragmentor set to 175 V and the mass range is 100-800 Da; Pos mode→ Gas temperature set to 180^{o}C, with 8.5 L/ min flow, Vcap-1100V, fragmentor set to 175 V and the mass range is 100-1000. The instrument was calibrated with the calibration solution provided by Agilent and calibration was performed before the source switching. Data acquisition was conducted using MassHunter LC/MS Data Acquisition software (Version B.05.01) and spectrum averaging, background subtraction and peak list generation were done by Agilent MassHunter Qualitative analysis (Version B.06.00) software.

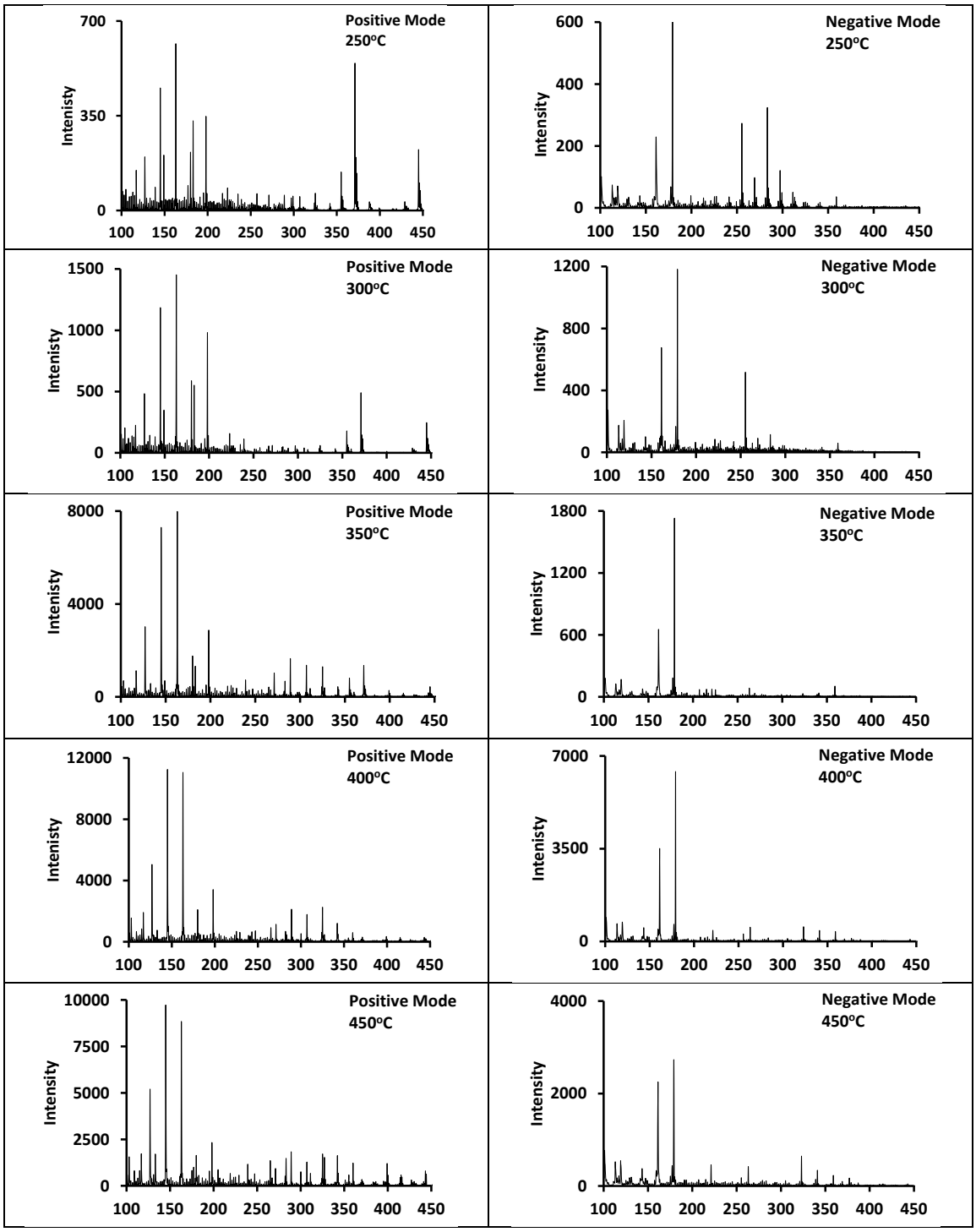

Fig. S1. DART temperature effects for endotoxin in both positive (left panel) and negative ion modes (right panel). Shown are mass spectra acquired for 1 µL 0.62 ng mL^{-1} endotoxin solutions at different DART helium temperatures of 250°C, 300 °C, 350 °C, 400 °C and 450 °C in positive and negative ion modes, respectively.

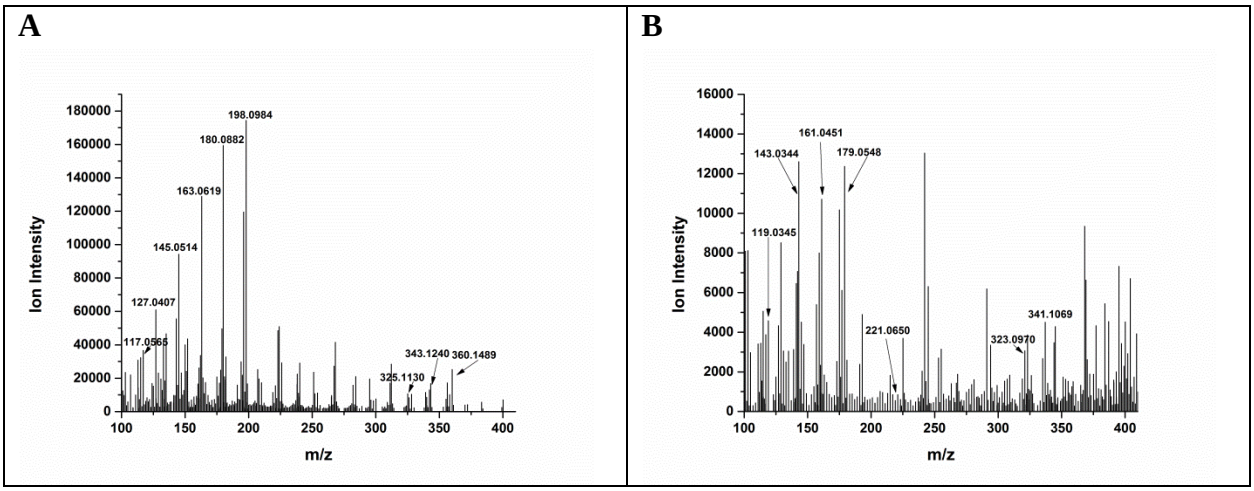

Fig. S2. Mass spectra of endotoxin standards acquired from DART coupled to a high resolution Q-TOF mass spectrometers in (A) positive mode and (B) negative mode.

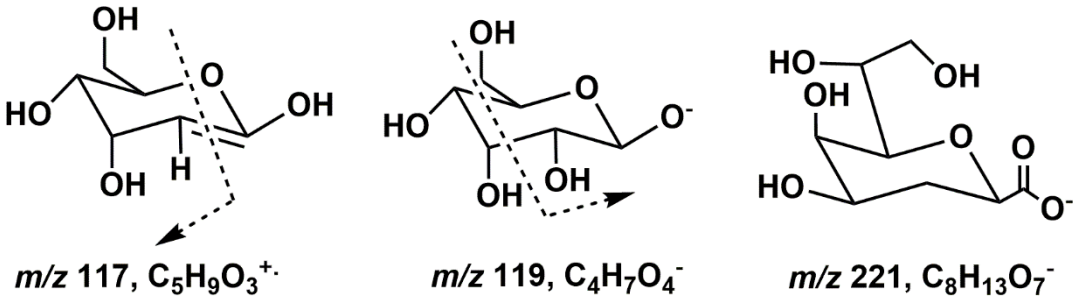

Fig. S3. Proposed structures for ions of *m/z* 117, *m/z* 119 and *m/z* 221 as listed in Table 1.

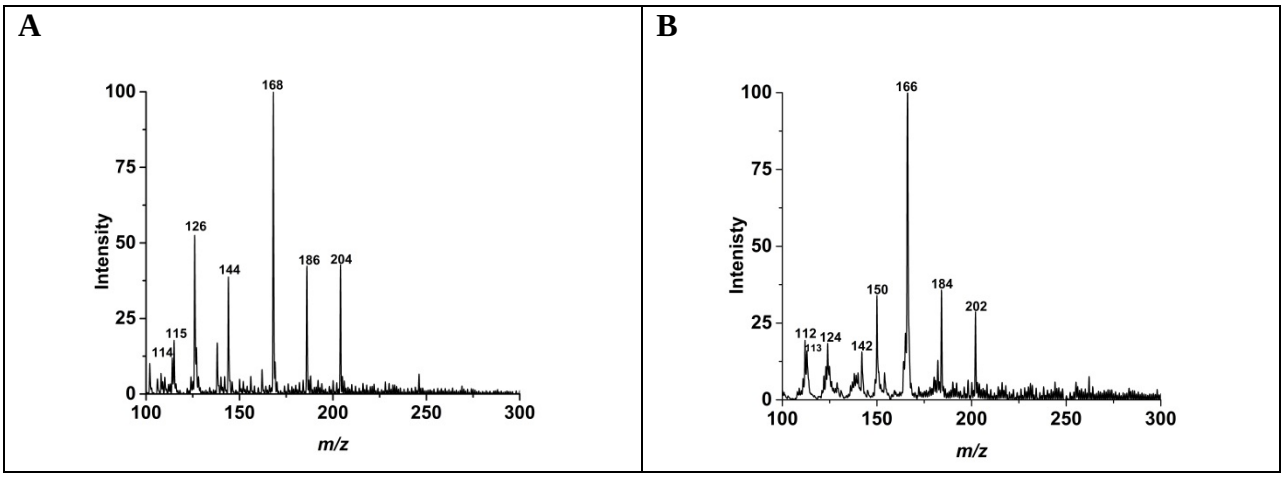

Fig. S4. Mass spectra for NaHA standard in positive (A) and negative ion (B) modes, where 10 mg mL^{-1} NaHA OVD fluid was diluted using 50:50 methanol and water with 1:5 (w:w) ratio.

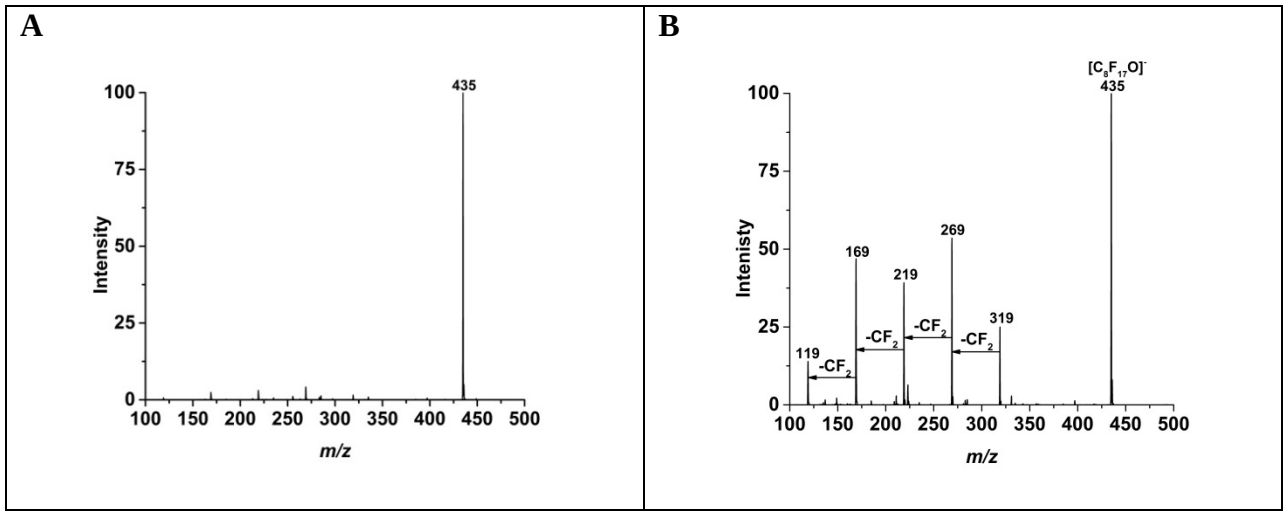

Fig. S5. Mass spectra for perfluoro-n-octane (PFO) without fragmentation (A) and with fragmentation (B) in negative ion mode. Spectrum B shows the 30 V in-source fragmentation, producing sequential loss of CF_2 as major fragment ions.

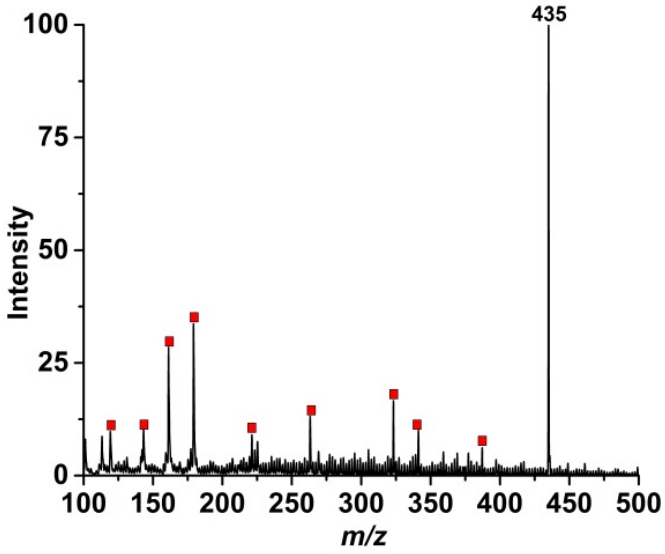

Fig. S6. Mass spectrum acquired for the mixture of endotoxin and perfluoro-n-octane (PFO) in negative ion mode. 1 µL PFO was pipetted on top of 1 µL of 1.25 ng mL^{-1} of aqueous endotoxin on a dip-it-tip, and the mixture was analyzed by DART-MS immediately through manual sampling. No fragmentation energy was employed in this example and red squares indicate the major endotoxin signals at 400^{o}C DART analysis.

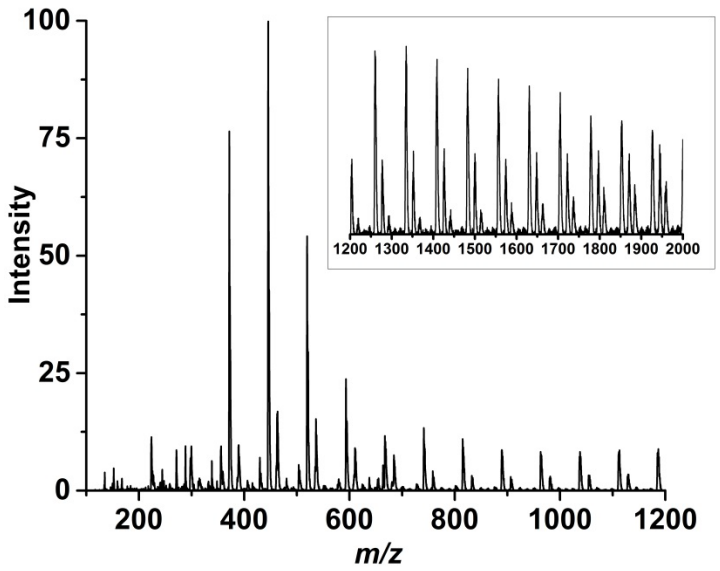

Fig. S7. Mass spectrum obtained for polydimethylsiloxane (silicone oil) standard in positive ion mode. 2 µL of 1 to 100 dilution of silicone oil in hexane was applied to the bottom of dip-it tip. Inserted window shows the extended mass range up to *m/z* 2000. Characteristic SiO $(CH_3)_2$ loss was detected for silicone oil across the mass range.