Supplementary Material (ESI) for Chemical Communications

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"Ambient generation of fatty acid methyl ester ions from bacterial whole cells by direct analysis in real time (DART) mass spectrometry", by Carrie Y. Pierce, John R. Barr, Robert B. Cody, Robert F. Massung, Adrian R. Woolfitt, Hercules Moura, Herbert A. Thompson and Facundo M. Fernandez.

Summary of Other Ambient Ionization Methods:

DESI and DART are two of several high throughput open air ionization methods that have been recently described. Cooks et al. have reported a desorption ionization method with some common features with DART, which they named desorption atmospheric pressurec chemical ionization (DAPCI)[1]. McEwen et al.have described a modified atmospheric pressure chemical ionization technique for the direct analysis of solids, which they named atmospheric-pressure solids analysis probe (ASAP)[2]. Shiea et al. almost simultaneously described electrospray-assisted laser desorption ionization (ELDI), a method that combines laser desorption, and neutral post-ionization by charged electrospray droplets[3, 4]. More recently, Eberlin et al reported a (high) voltage free ambient desorption ionization method which they named desorption sonic spray ionization. (DeSSI)[5].

1. Z. Takats, I. Cotte-Rodriguez, N. Talaty, H. W. Chen and R. G. Cooks, *Chem. Commun.*, 2005, **15**, 1950-1952.
2. C. N. McEwen, R. G. McKay and B. S. Larsen, *Anal. Chem.*, 2005, **77**, 7826-7831.
3. J. Shiea, M. Z. Huang, H. J. HSu, C. Y. Lee, C. H. Yuan, I. Beech and J. Sunner, *Rapid Commun. Mass Spectrom.*, 2005, **19**, 3701-3704.
4. M. Z. Huang, H. J. HSu, J. Y. Lee, J. Jeng and J. Shiea, *J. Proteome Res.*, 2006, **5**, 1107-1116.
5. R. Haddad, R. Sparrapan and M. N. Eberlin, *Rapid Commun. Mass Spectrom.*, 2006, **20**, 2901-2905.

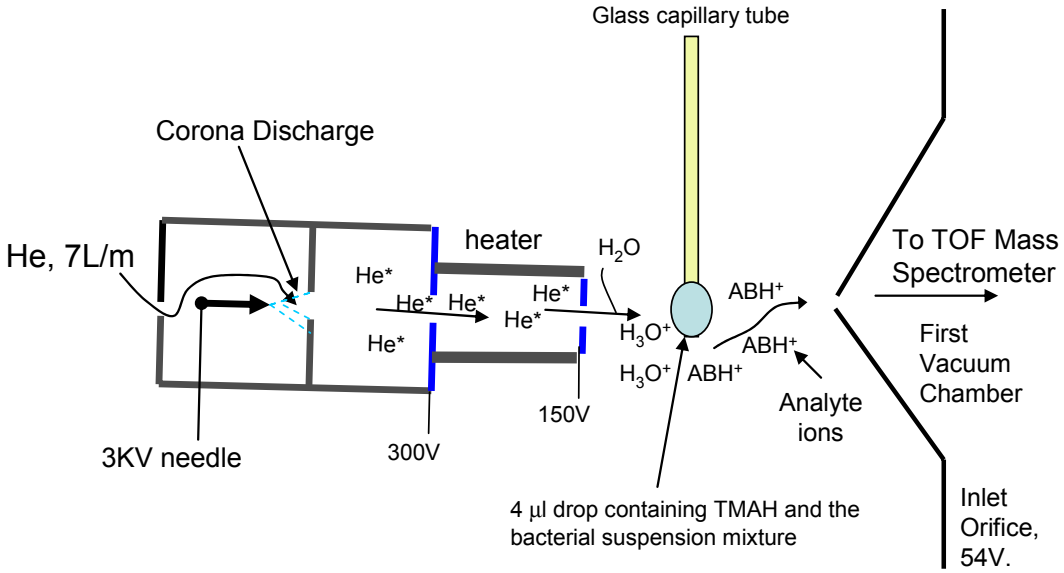

Figure S-1: Schematic of the DART TOF MS setup for the analysis of bacterial suspensions (parts not to scale). Sliding arm and aligator clip securing the glass capillary are not shown for simplicity.

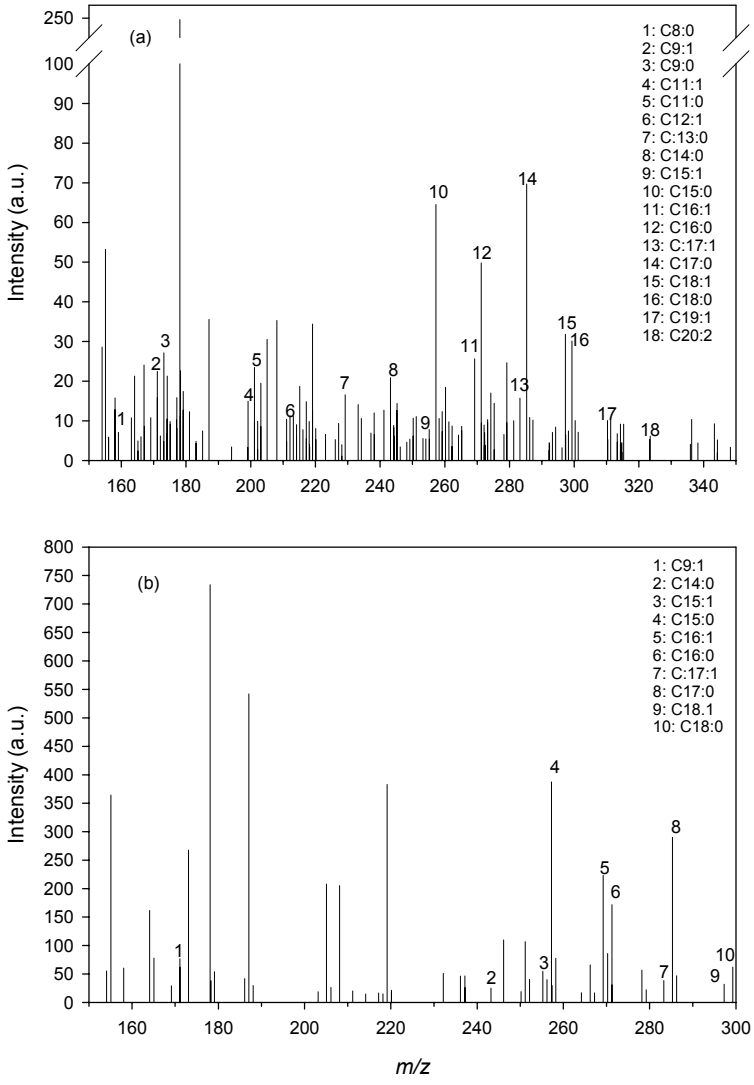

Figure S-2 (a) Positive ion mass spectrum of *C. burnetii* Nine Mile II (Gram negative) acquired by DART-TOF MS analysis of *in-situ* thermal hydrolysis/methylation ionization of the bacterial membrane fatty acids to generate the corresponding fatty acid methyl esters (FAMEs). **(b)** Positive ion mass spectrum of *C. burnetii* RSA 514 (Gram negative).

Table S1 Comparison of bacterial fatty acid relative abundances for *E. coli, S. pyogenes,* and *C. burnetii* (Nine Mile I strain).

Fatty acid	Theor. *m/z*	Abundance (Δ mass [mmu])		
		E.coli	*S. pyogenes*	*C. burnetii*
C8:1	157.1229	5.2 [6]	14.3 [8]	3.9 [14]
C8:0	159.1385	8.0 [12]	10.6 [4]	7.2 [10]
C9:1	171.1385	2.3 [10]	2.1 [6]	9.7 [14]
C9:0	173.1542	4.9 [9]	-	19.6 [10]
C10:1	185.1542	2.8 [3]	3.5 [10]	5.6 [2]
C10:0	187.1698	3.9 [8]	-	-
C11:1	199.1698	-	4.4 [11]	-
C11:0	201.1855	3.0 [9]	-	-
C12:1	213.1855	2.5 [4]	1.8 [12]	-
C12:0	215.2011	2.9 [5]	-	15.4 [12]
C14:1	241.2168	1.3 [6]	1.6 [7]	-
C14:0	243.2324	3.5 [2]	-	11.2 [1]
C15:1	255.2324	-	-	19.0 [2]
C15:0	257.2481	4.1 [4]	-	38.7 [1]
C16:1	269.2481	10.6 [5]	24.0 [3]	2.5 [6]
C16:0	271.2637	17.6 [4]	19.1 [2]	28.1 [2]
C17:1[a]	283.2637	21.7 [4]	-	-
C17:0	285.2794	-	-	31.2 [1]
C18:2	295.2637	0.5 [9]	3.4 [5]	-
C18:1	297.2794	6.9 [6]	31.8 [2]	3.2 [2]
C18:0	299.2950	-	-	7.7 [3]
C19:1[a]	311.2950	12.9 [6]	-	-
C19:0	313.3107	-	-	7.1 [7]
C21:1	339.3263	-	-	1.3 [1]
C21:0	341.3400	-	-	4.4 [9]
C24:1	381.3733	-	-	1.4 [6]
C24:0	383.3889	-	-	1.3 [10]

[a] Cyclopropyl fatty acids are common constituents of bacterial lipids. CycloC17:0 and cycloC19:0 accurate masses are identical to that of the monoenoic fatty acids C17:1 and C19:1 respectively, and thus could not be differentiated.