Electronic Supplementary Material (ESI) for RSC Advances.

Rapid recognition of bacteremia in humans using atmospheric pressure chemical ionization mass spectrometry of volatiles emitted by blood cultures

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SUPPORTING INFORMATION

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Figures and Tables

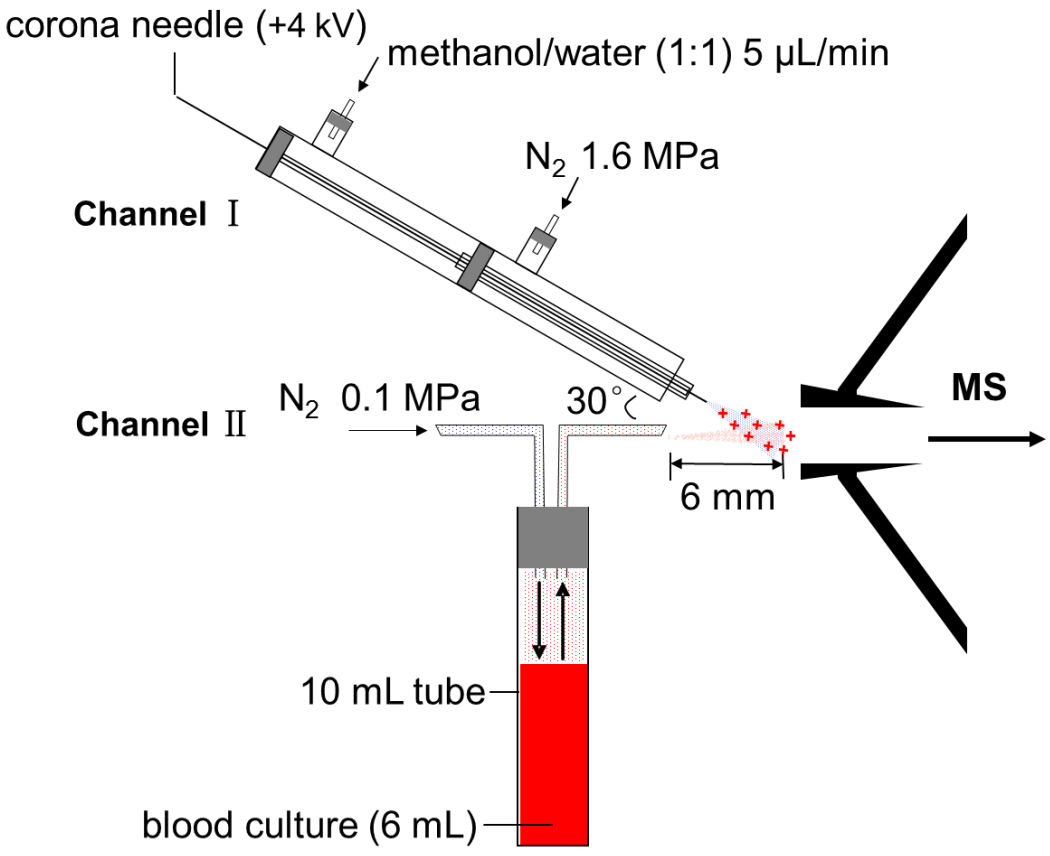

Fig. S1 Headspace VOC analysis of blood cultures by APCI-MS.

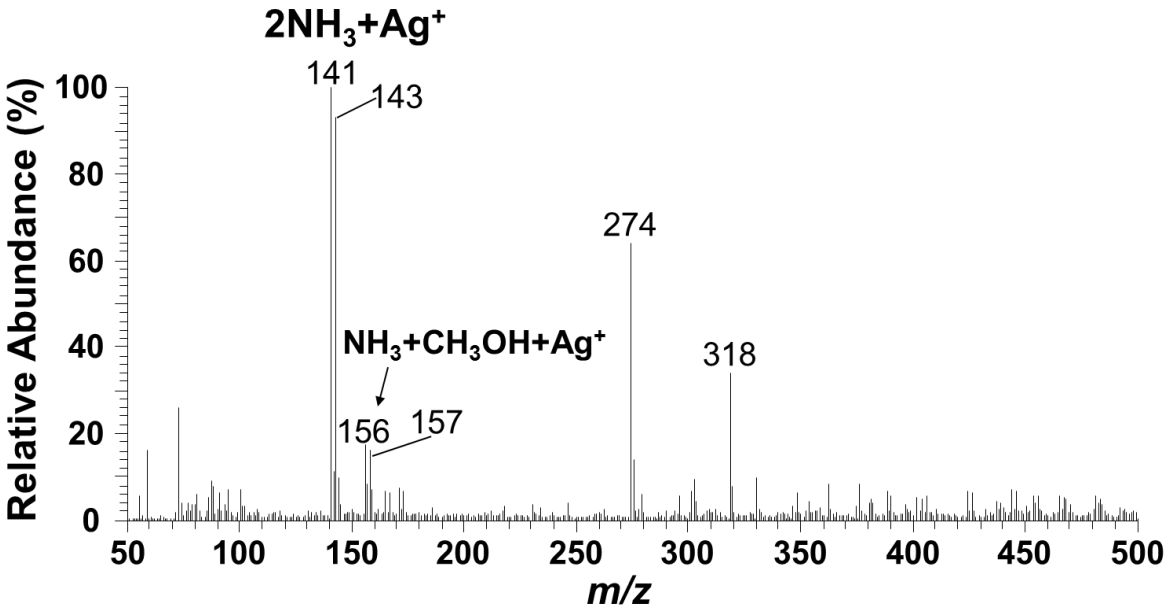

Fig. S2 EESI-MS spectrum for PA blood cultures using gas-phase Ag^+ as primary ions for ionization. Methanol solution of $AgNO_3$ (100 μM) was used as a source of Ag^+ ions. Signals at *m/z* 274, *m/z* 318 as well as some non-labeled signals in low mass range also occur in EESI-MS of blank air and likely correspond to methanol clusters.

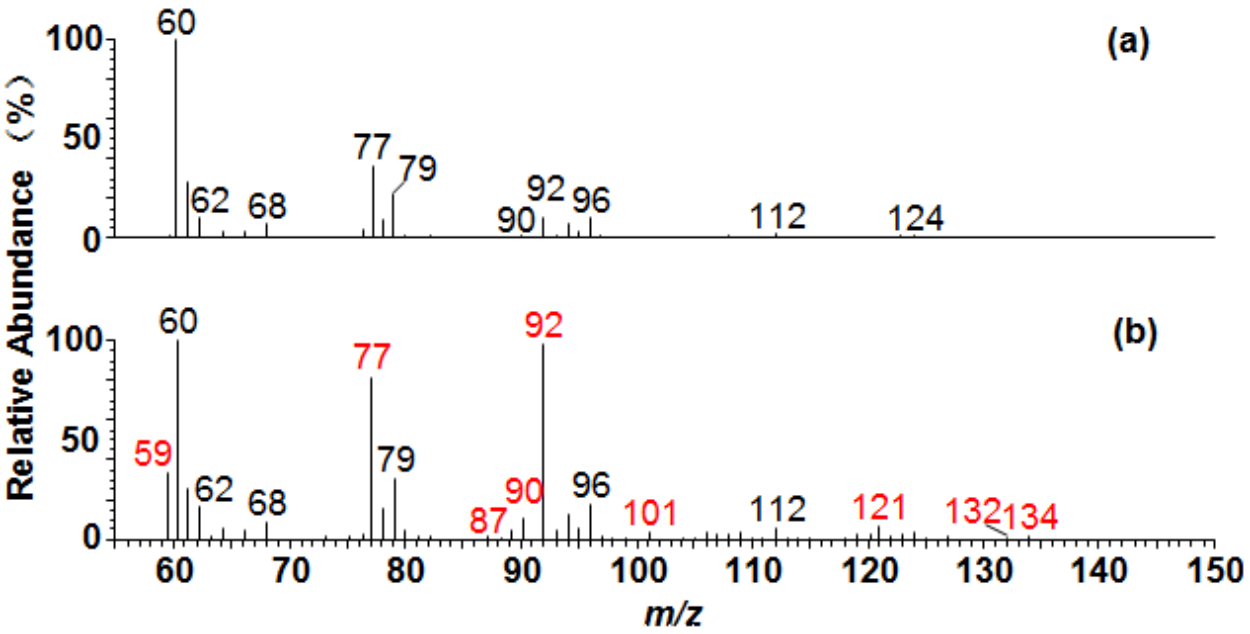

Fig. S3 Negative ion polarity APCI-MS of air from the headspace of an empty centrifuge tube (a) and the headspace of the same tube with blood culture of a patient with PA bacteremia diagnosed after 16 h incubation (b). The red font color corresponds to PA biomarker signals.

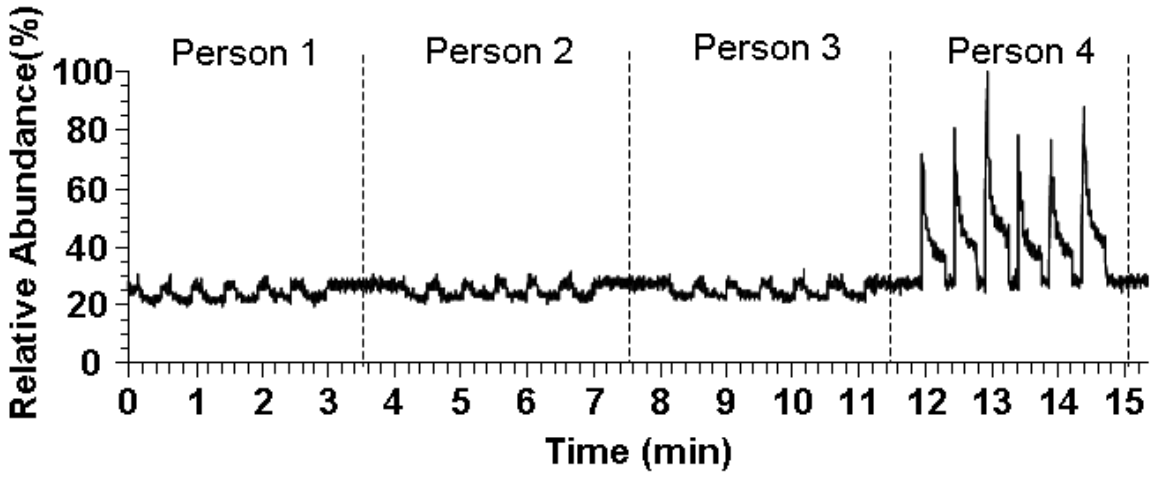

Fig. S4 Inter-individual difference occurring in the intensity of signal at *m/z* 80 by APCI-MS analysis of non-inoculated blood cultures.

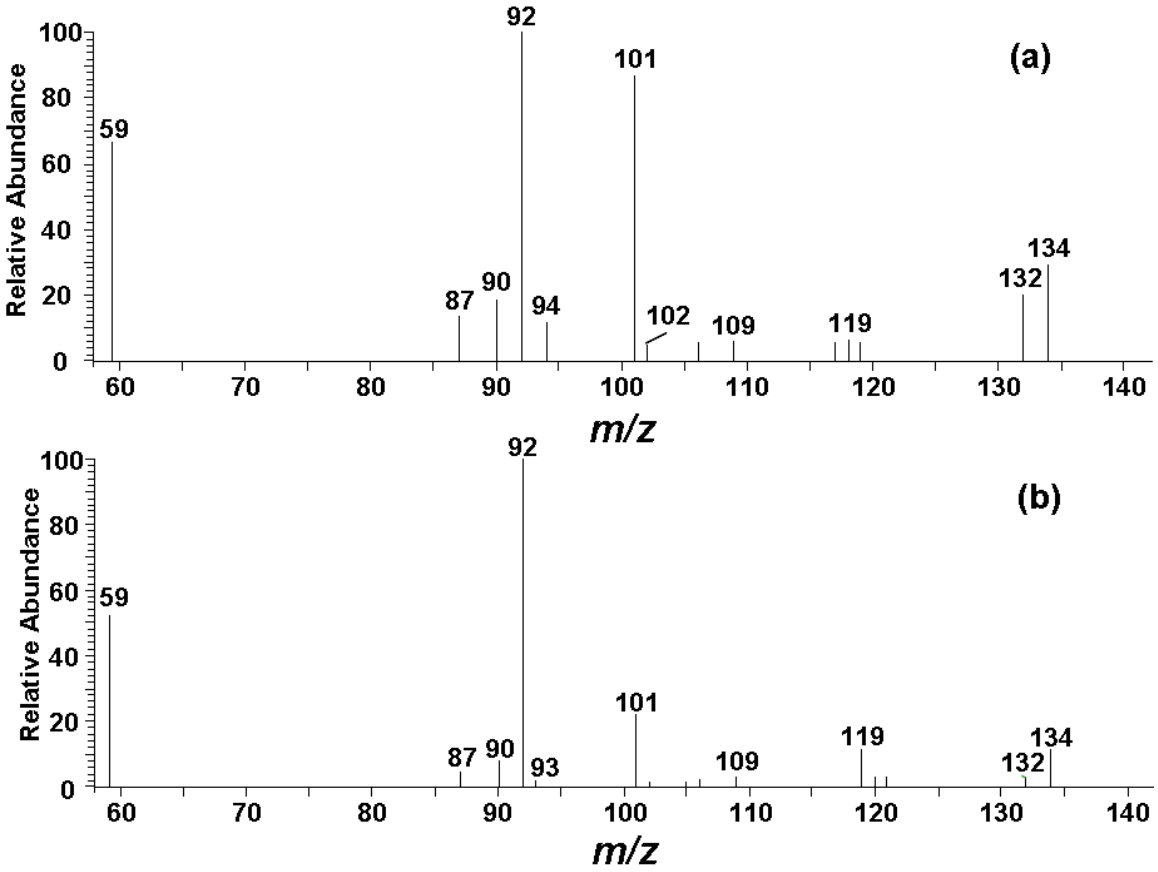

Fig. S5 VOC fingerprints of simulated SA blood culture incubated for 16 h in TSB (a) and in blood/TSB mixture (b).

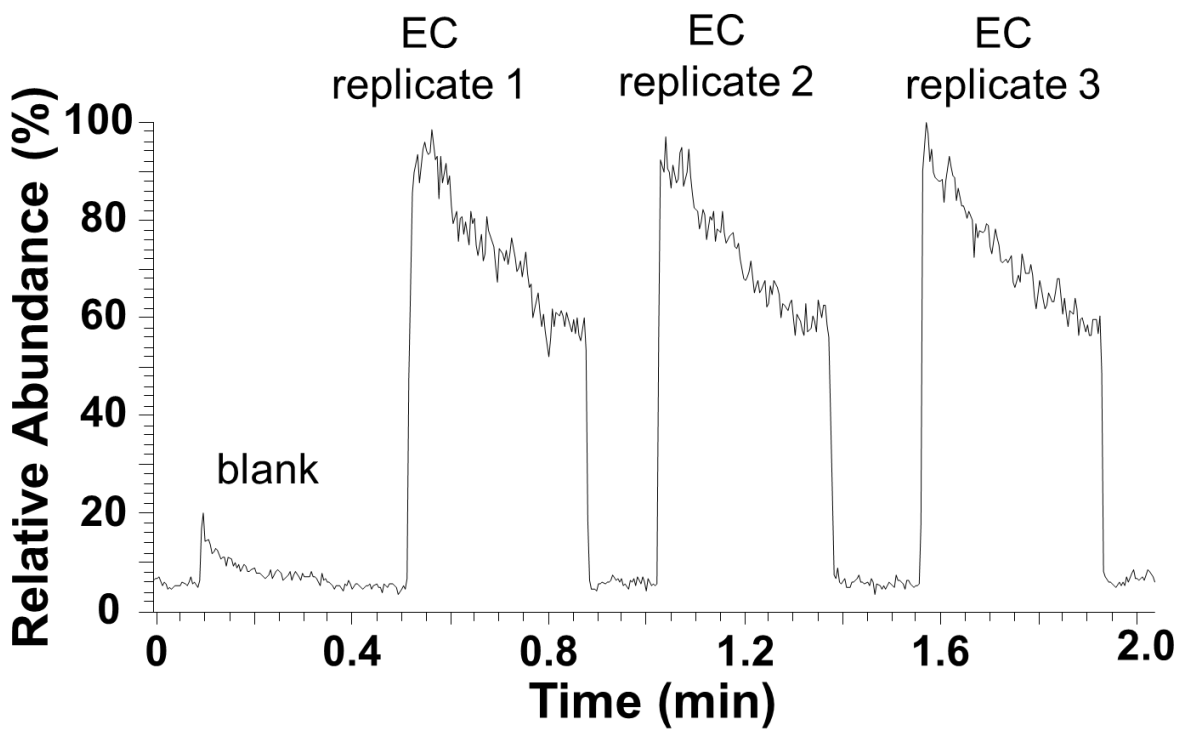

Fig. S6 Successive samplings of three technical replicates for EC grown in TSB (without blood), showing good reproducibility of signal intensity in APCI-MS.

Table S-1. Summary of VOC signals observed in bacterial blood cultures by APCI-MS. SA = *Staphylococcus aureus*, EC = *Escherichia coli*, KP = *Klebsiella pneumonia*, AB = *Acinetobacter baumannii*, PA = *Pseudomonas aeruginosa.* Chemical assignments were done based on the match with reference MS/MS measurements of standard compounds.* Chemical assignments were further verified based on the earlier MS reports of volatile bacterial pathogens summarized in L. D. J. Bos, P. J. Sterk and M. J. Schultz, *PLoS Pathog*., 2013, 9, e1003311. Signals that did not yield notable fragments within the detection window are marked as "-". Relative signal intensities in MS fingerprints of each bacterium are marked as follows: "+++++" = 80%-100% relative intensity; "++++" = 60%-80%; "+++" = 40%-60%; "++" = 20%-40%; "+" = 0%-20%.

m/z	**PA**	**AB**	**SA**	**KP**	**EC**	**MS/MS transitions (identification)**
Positive ion detection mode						
60	+	++				*m/z* 45, *m/z* 44 (trimethylamine)
63		+++++		+++	+	*m/z* 47, *m/z* 45, *m/z* 43
64			+++++	+++++	+++++	–
65			++		+	–
70	+++++					*m/z* 43, *m/z* 28 (1-vinyl aziridine)*
74				+	+	*m/z* 56, *m/z* 46, *m/z* 32
78	+	+		+	+	–
84	+		+		+	*m/z* 67, *m/z* 56, *m/z* 42, *m/z* 30
88		+				–
100	+					–
104				+	+	–
106			+			–
118					++	*m/z* 101, *m/z* 100, *m/z* 72 (indole)
123		+	+			–
Negative ion detection mode						
59	+++	+++	+++	+++	+++	–
73		+				*m/z* 45, *m/z* 35
77		++	+			–
87			+++			*m/z* 59, 43 (butyric acid)*
90	++	++	++	++	++	–
92	+++++	+++++	+++++	+++++	+++++	*m/z* 76, *m/z* 59, *m/z* 46
93	+	+	+	+		–
101			++++			*m/z* 83, *m/z* 73, *m/z* 57 (isovaleric acid)
106				+		–

116					+	*m/z* 98, *m/z* 87, *m/z* 72 (indole)
119	+	+		+		*m/z* 59 (acetic acid cluster)**
121	++	++	++	++		–
132			+			isovaleric acid cluster**
134			+			isovaleric acid cluster**

*The reference MS/MS spectra for 1-vinyl aziridine and butyric acid were not recorded due to the lack of commercially available standard. Tentative chemical assignment of *m/z* 70 signal to 1-vinyl aziridine was done based on the earlier reported data for PA VOCs by W. Filipiak, A. Sponring, M. Baur, A. Filipiak, C. Ager, H. Wiesenhofer, M. Nagl, J. Troppmair and A. Amann, *BMC Microbiol.*, 2012, 12, 1-16. Tentative assignment of *m/z* 87 to butyric acid was done based on the available MS/MS reports in the literature (summarized in L. D. J. Bos, P. J. Sterk and M. J. Schultz, *PLoS Pathog*., 2013, 9, e1003311).

**Some compounds produced more than one signal in APCI-MS, presumably due to cluster formation during ionization.