Electronic Supplementary Material (ESI) for Analyst.

Supporting Information for

Time Resolved Growth of (N)-Polycyclic Aromatic Hydrocarbons in Engine Deposits Uncovered with OrbiSIMS Depth Profiling

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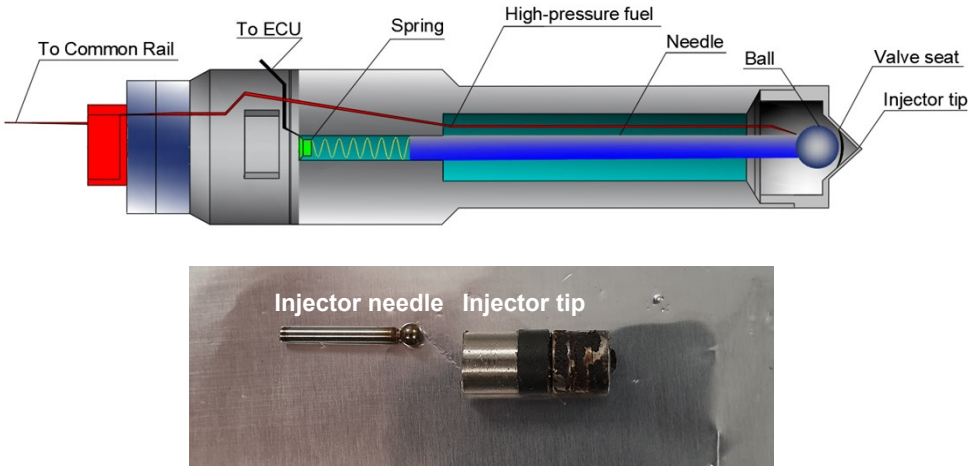
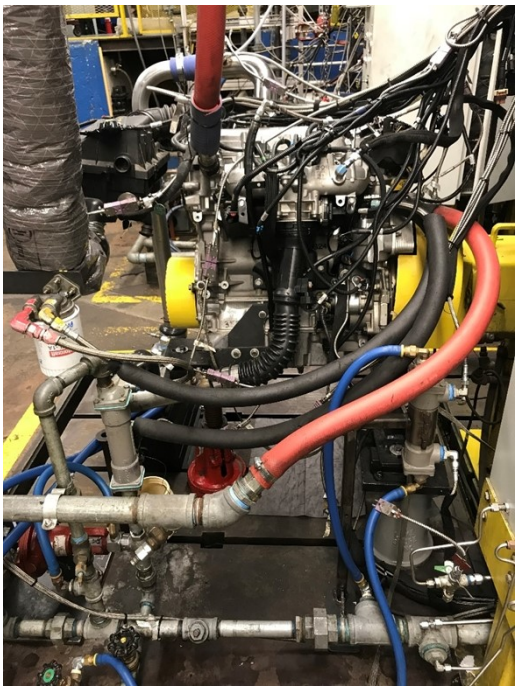
S1

(a)


To Common Rail
To ECU
Spring
High-pressure fuel
Needle
Ball
Valve seat
Injector tip
Injector needle
Injector tip

(b)



(c)

Fuel injector set	origin	Gasoline type/tier	alcohols		paraffins			olefins			benzene rings			napht-halenes	indene		
			ethanol	larger alcohols	linear	branched	cyclic	linear	branched	cyclic	toluene	with paraffinic chains	with olefinic chains		indene	with paraffinic chains	with olefinic chains
Injector 1*	Corpus Christi, TX, USA	Standard retail E10	present	present	present	present	present	present	present	not present	present	present	present	present	not present	not present	not present
Injector 2	USA	Standard retail E10	present	present	present	present	present	not present	present	present	present	present	present	present	not present	present	not present
Injector 3*	Martinez, CA, USA	Standard retail E10	present	present	present	present	present	present	present	present	present	present	present	present	not present	not present	not present
Injector 4*	Baton Rouge, LA, USA	Standard retail E10	present	present	present	present	present	present	present	present	present	present	present	present	not present	present	not present
Injector 5	USA	Standard retail E10	present	present	present	present	present	present	present	not present	present	present	present	present	not present	not present	not present
Injector 6*	Richmond, CA, USA	Standard retail E10	present	present	present	present	present	present	present	not present	present	present	present	not present	not present	not present	not present
Injector 7	USA	EEE Lube certificat-ion	Unknown														
Injector 8	USA	US ‘top tier’ retail E10															

* Quantified data available in data repository

present

not present

Fig. S1. (a) Schematic of a gasoline direct injection unit (above), photographs of injector tip and needle 1 as an example of the components studied in this work (below). **(b)** Photographs of the engine testing rig used to generate the deposits used in this work. Images provided courtesy of Intertek USA. **(c)** Summary of the composition of fuel used in the deposit formation engine test acquired from GC-EI-MS analysis. The quantified information is unknown but adhered to USA fuel specification.[1] Injectors 1-6 were retrieved from engine testing using one fuel. E10, 10 % ethanol containing.

Table S2. Experimental 3D OrbiSIMS parameters that varied on all samples. Common parameters are detailed in the methods. **(a)** Injector tip samples, including full depth profiles and 'depth profile & imaging' experiments. **(b)** Injector needle samples.

(a)

	Parameter	Tip 1		Tip 2		Tip 3		Tip 4		Tip 5		Tip 6		Tip 7		Tip 8	
		+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-
Depth profile	Sputter time (s)	8000	34300	85000	128000	49430	122420	35315	10151	17379	8222	4543	30666	11992	6015	34131	22094
	Total dose (ions)	5.5×10^{12}	2.5×10^{13}	1.9×10^{14}	1.8×10^{14}	3.51×10^{13}	2.54×10^{13}	5.5×10^{13}	1.58×10^{13}	2.49×10^{13}	1.18×10^{13}	3.23×10^{12}	4.71×10^{13}	2.1×10^{13}	1.05×10^{13}	5.54×10^{13}	3.58×10^{13}
	Analysis area μm²	200	200	400	300	200	50	200		200		200		200		200	
	Target current (pA)	219	230	238	238	233	230	250		230		248		280		260	
	Raster mode	sawtooth		sawtooth		random		random		random		random		random		random	
Combined imaging & depth profile	Sputter polarity	-		+		+											
	Analysis area (μm²)	200		150		150											
	Total sputter time (s)	510		2650		1860											
	Total dose (ions)	5.25×10^{11}		1.52×10^{12}		1.11×10^{12}											
	Image scans	2		3		3											
	Pixels	60 × 60		30 × 30		30 × 30											
	Image area (μm²)	300															
	Raster mode	random															

(b)

	Parameter	Needle 1		Needle 2		Needle 3		Needle 4		Needle 5		Needle 6		Needle 7		Needle 8	
		+	-	+	-	+	-	+	-	+	-	+	-	+	-	+	-
Depth profile	Sputter time (s)	911	2786	1069	978	1622	3762	122	370	245	745	511	887	204	239	120	561
	Total dose (ions)	6.2×10^{11}	?	7.27×10^{11}	6.80×10^{11}	1.15×10^{12}	2.56×10^{12}	3.60×10^{11}	1.09×10^{12}	3.53×10^{11}	1.07×10^{12}	7.31×10^{11}	1.27×10^{12}	2.93×10^{11}	3.42×10^{11}	1.73×10^{11}	8.05×10^{11}
	Analysis area (μm²)	200		200		200		200		200		200		200		200	
	Primary ion current (pA)	220		220		220		235		230		230		230		230	
	Raster mode	random		random		random		random		random		random		random		random	

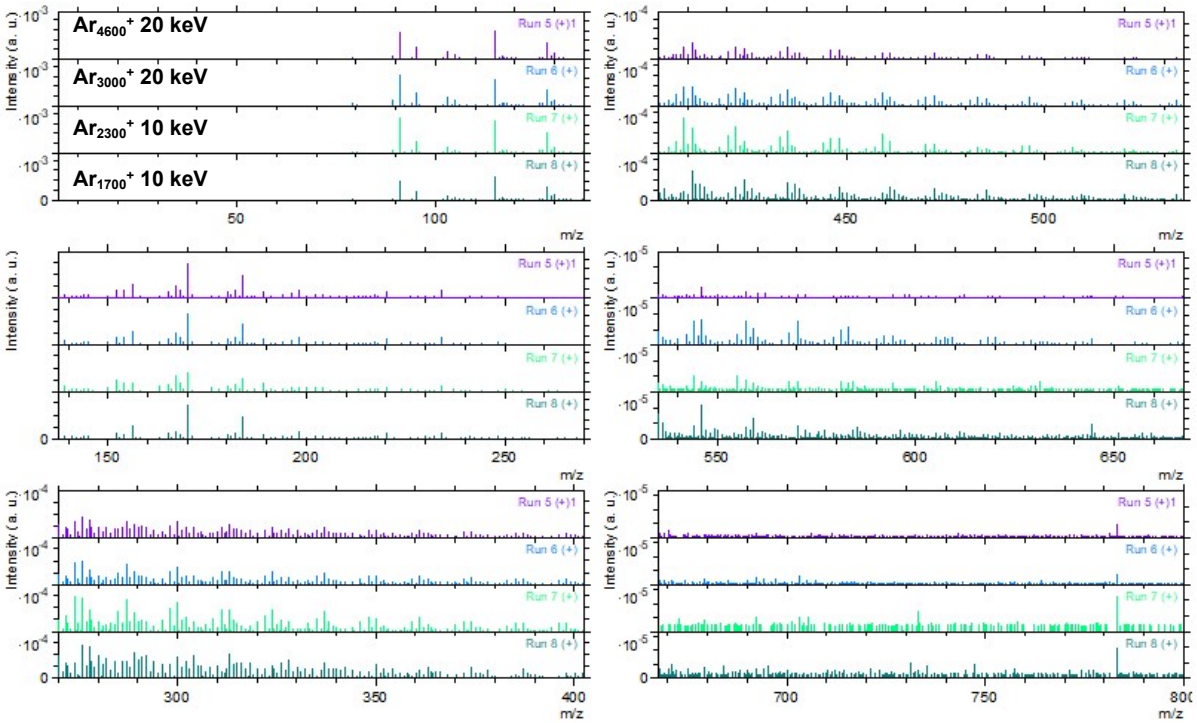
S3 – Optimization experiments

Before conducting extensive analysis with 3D OrbiSIMS we investigated the effect on ion intensity and chemical speciation (particularly of positively ionizing carbonaceous species) by altering key analysis settings. The aim of this work is to achieve maximum secondary ion intensity without affecting speciation of known species in deposits. We performed analytical repeats of depth profiles on injector tip 3 by carrying out short depth profiles (10 s) in one analysis area using different instrumental settings. We altered ion source & energy, pressure of nitrogen flow and argon flow for charge compensation, and flood gun energy. In each case the best setting was compared to the last and carried forward into the next experiment (**table S3a**). We kept analysis times short to prevent sputtering into layers with different deposit chemistry, datasets were only compared with the next in sequence, so we were observing comparable chemistries with < 20 s difference in sputtering (accounting for both polarities). Previous work found that it took up to two days of sputtering to reach the lowest deposit layer.[2] We found that Ar_{3000}^+ gave the best overall ion intensity in both polarities compared to larger and smaller cluster sizes/energies (**fig. S3bi**). Negative polarity mode also showed a far lower peak intensity when cluster size was altered from Ar_{3000}^+ (**fig. S3bii**). This agrees with previous work which explored the ideal cluster size for homogeneous organic reference materials.[3,4] An Ar flooding pressure of 1 x 10^{-6} mbar (the setting used so far in this work), which is used to delocalize charge surrounding the analysis area,[5] was ideal for identifying PAHs of high mass (> *m/z* 500) (**fig. S3bi**). Intensity of negative ions varied when the flood pressure was increased, for example the parent ion of alkyl benzyl sulfonates, identified in previous work ($C_{18}H_{29}SO_3^-$, *m/z* 325.18),[2] had higher intensity with less Ar flooding, and its fragments (SO_3^-, *m/z* 80.01 & $C_8H_7SO_3^-$, *m/z* 183.01) had lower intensity (**fig. S3cii**). Other settings (**fig. S3a**) yielded insignificant changes to the ion intensity or chemical speciation (data not shown). Importantly there is little difference in the speciation of carbonaceous material including PAHs. This further ratifies the method and instrument parameters used in this and previous work.[2]

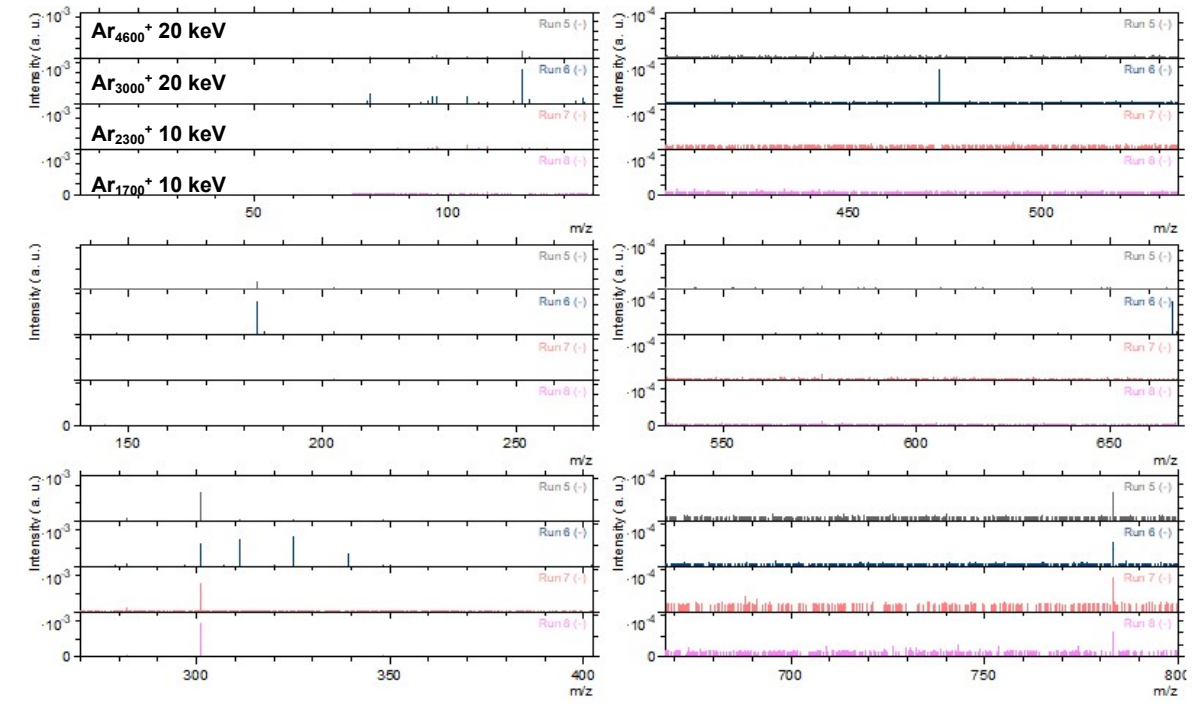
(a)

		Experiment number & parameter Investigated										
		1	2	3	4	5	6	7	8	9	10	11
Ion beam energy and cluster size	20 kV, Ar_{3000}^+	x	x	x			x			x	x	x
	20 kV, Ar_{2300}^+							x				
	10 kV, Ar_{1700}^+								x			
	20 kV, Ar_{4600}^+				x	x						
N pressure (bar)	12					x	x	x	x	x	x	x
	10	x	x	x	x							
Flood gun energy	21 V	x										
	10 V		x		x	x	x	x	x	x	x	x
	10 V low anode			x								
Ar pressure (mbar)	1.00×10^{-6}	x	x	x	x	x	x	x	x			
	1.00×10^{-5}									x		
	1.00×10^{-7}										x	
	OFF											x

(b) i.



ii.


Ar4600+ 20 keV
Ar3000+ 20 keV
Ar2300+ 10 keV
Ar1700+ 10 keV
Run 5 (-)
Run 6 (-)
Run 7 (-)
Run 8 (-)
Intensity (a. u.)
m/z

(c) i.

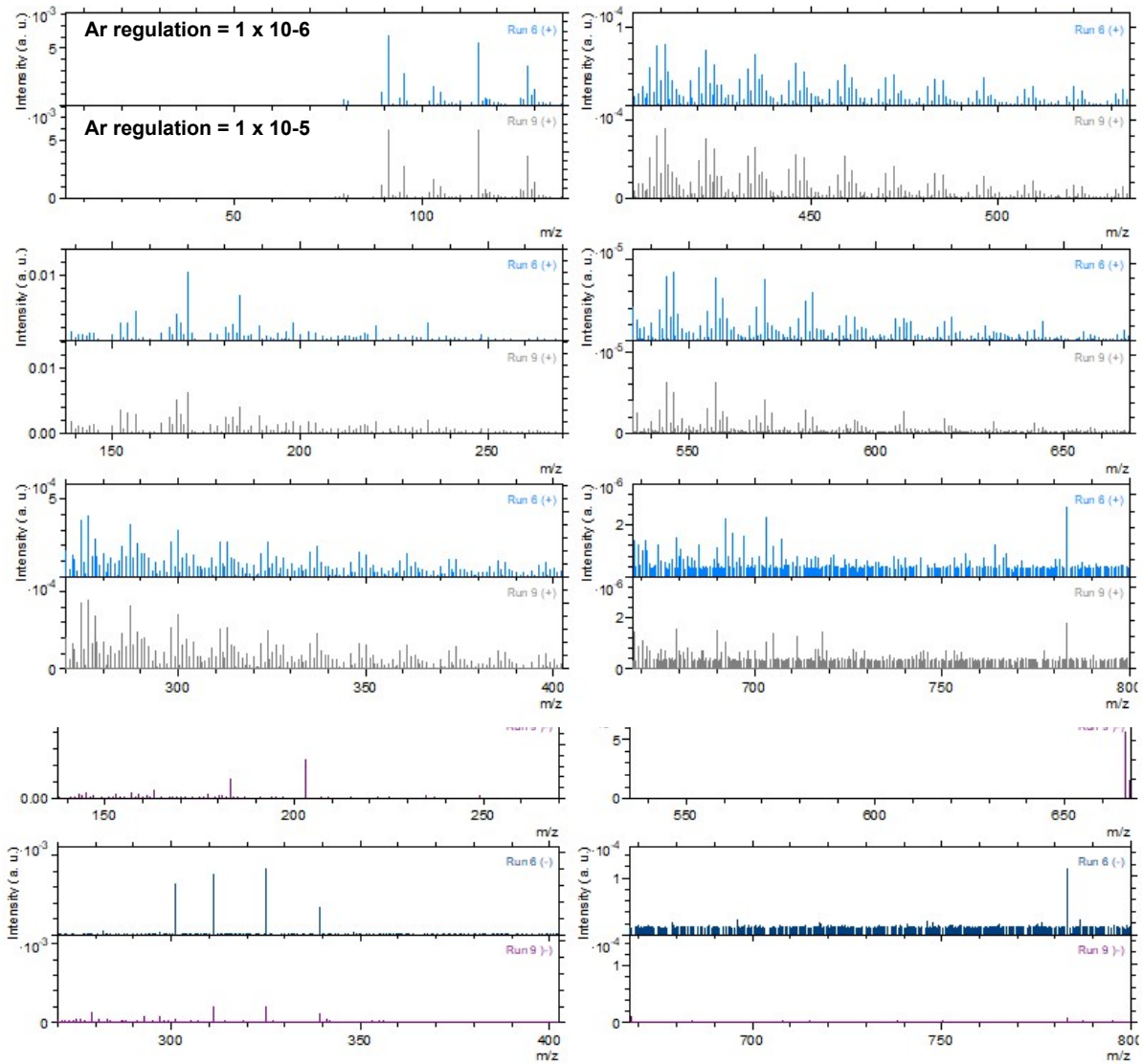

Ar regulation = 1 x 10-6
Ar regulation = 1 x 10-5
Run 6 (+)
Run 9 (+)
Run 6 (-)
Run 9 (-)
Intensity (a. u.)
m/z

Fig. S3: **(a)** Table of experiments summarizing the interchangeable settings used, carried out on the deposit on injector tip 3. In each case a 10 s depth profile was carried out in both polarities. Green boxes represent the most ideal settings determined. **(b)** Comparing the effects of cluster size on the ion intensity and speciation for **i.** positive ions and **ii.** negative ions. Cluster sizes are displayed in the first mass window and are consistent for others. **(c)** Comparing the effects of Ar flood pressure (lower pressure = upper spectra, higher pressure = lower spectra) on the ion intensity and speciation for **i.** positive ions and **ii.** negative ions.

Table S4. 3D OrbiSIMS accurate mass ion table for negative ions identified in **(a)** injector tip deposits, **(b)** injector needle deposits All ion peak tables were exported from Surface Lab software (IONTOF GmbH, version 7.1.b). Deviation (ppm) refers to the difference between the observed and expected ion mass. The observed mass is measured as the center mass of the ion peak.

(a)

	Injector tip 1			Injector tip 2			Injector tip 3			Injector tip 4		
Formula	Centre Mass (u)	Deviation (ppm)	Area	Centre Mass (u)	Deviation (ppm)	Area	Centre Mass (u)	Deviation (ppm)	Area	Centre Mass (u)	Deviation (ppm)	Area
Linear carboxylic acids												
C_16H_31O_2-	255.233584	2.468516	50086698	255.233336	1.498798	21786870	255.233479	2.058172	78645	255.233119	0.648538	9023913.7
C_18H_35O_2-	283.264906	2.301217	84017259	283.264585	1.168911	29131807	283.264475	0.779082	99461	283.264379	0.442219	9945651.6
alkyl benzyl sulfonate												
C_8H_7SO_3-	183.01236	1.213189	399902141	183.012143	0.025332	141536538	183.012234	0.523136	4834713	183.012097	-0.226048	395473361
C_17H_27SO_3-	311.169216	1.855658	70336741	311.16893	0.935851	14549883	311.168948	0.993089	552765	311.168824	0.594391	68874475
C_18H_29SO_3-	325.184685	1.217576	79811853	325.184363	0.227101	16971174	325.184507	0.670856	517889	325.184333	0.135293	66890572
Alkyl salicylate												
C_7H_5O_3-	137.024529	0.80966	16644925	137.024397	-0.150398	25384207	137.024403	-0.103103	1770285	137.024329	-0.645321	39319868
C_8H_7O_3-	151.040165	0.647327	10203394	151.040047	-0.136584	14535173	151.040055	-0.082127	852242	151.039962	-0.6973	16274609
C_9H_9O_3-	165.055796	0.474686	4214774	165.055694	-0.14192	4849130	165.0557	-0.105381	173366	165.055587	-0.789488	3685157.3
C_10H_11O_3-	179.071531	0.909078	1577751	179.071424	0.313803	1039881	179.071419	0.286865	26959	179.071316	-0.291531	752593.23
C_11H_13O_3-	193.087151	0.688197	510866	193.087056	0.197871	242533	193.087083	0.338146	6513	193.086937	-0.419875	117912.63
Fused salicylate												
C_11H_7O_3-	187.040223	0.831044	14221637	187.040116	0.260133	22303999	187.040113	0.240227	876828	187.039971	-0.517678	33280509
C_15H_9O_3-	237.056051	1.406505	5006857	237.055964	1.040837	16911459	237.055889	0.72434	381577	237.055707	-0.046611	11481717
C_19H_11O_3-	287.071957	2.052184	2759323	287.07176	1.366587	8058797	287.071631	0.916464	75028	287.071466	0.343286	4171746.5
Inorganic salts												
NaCl_2-	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	92.927915	-1.165	241238.22
CuCl-	97.899094	0.940184	26367	**x**	**x**	**x**	**x**	**x**	**x**	132.867826	-0.220729	2509513.6
FeCl_3-	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	160.84198	-0.426674	78836.73

	Injector tip 5			Injector tip 6			Injector tip 7			Injector tip 8		
Formula	Centre Mass (u)	Deviation (ppm)	Area	Centre Mass (u)	Deviation (ppm)	Area	Centre Mass (u)	Deviation (ppm)	Area	Centre Mass (u)	Deviation (ppm)	Area
Linear carboxylic acids												
C_16H_31O_2-	255.233262	1.20686	54308142.03	255.23304	0.337925	299352.31	255.233279	1.275937	14963596.2	255.233091	0.537181	1828903.87
C_18H_35O_2-	283.264516	0.926456	41285465.36	283.264288	0.121534	140512.28	283.264583	1.163223	17473572.77	283.264347	0.329323	1884037.29
alkyl benzyl sulfonate												
C_8H_7SO_3-	183.012169	0.169717	2486345453	183.012009	-0.70949	433640679	183.012229	0.497405	511434944.5	183.012084	-0.298616	71510485.24
C_17H_27SO_3-	311.168869	0.737874	229965508.9	311.168635	-0.013401	31251568.36	311.169047	1.310638	48850826.95	311.168803	0.52569	12471095.46
C_18H_29SO_3-	325.184382	0.284433	222058756.5	325.184171	-0.362732	30829940.28	325.18457	0.864633	43767912.32	325.18431	0.063479	10581554.48
Alkyl salicylate												
C_7H_5O_3-	137.024365	-0.387448	65032584.16	137.024285	-0.970042	95400107.47	137.024396	-0.160016	72399052.36	137.024308	-0.802657	32887063.29
C_8H_7O_3-	151.040013	-0.358782	32846961.37	151.039923	-0.9587	37560269.68	151.039998	-0.458912	14488279.81	151.039946	-0.807477	17425619.18
C_9H_9O_3-	165.055654	-0.383689	10458385.36	165.055562	-0.94458	7172130.37	165.055578	-0.844564	2202901.85	165.055579	-0.840663	4564124.62
C_10H_11O_3-	179.071382	0.082049	2374353.47	179.071284	-0.469488	860390.62	179.071321	-0.263784	225325.56	179.0713	-0.377747	837939.91
C_11H_13O_3-	193.087011	-0.037827	630588.52	193.086916	-0.528209	147144.48	193.086922	-0.497044	32373.17	193.086909	-0.565063	111938.79
Fused salicylate												
C_11H_7O_3-	187.040053	-0.079896	54001188.44	187.039948	-0.639915	82027502.44	187.039996	-0.384023	25939567.87	187.039959	-0.579344	17617872.44
C_15H_9O_3-	237.055841	0.521741	30061528.6	237.055666	-0.218618	66906255	237.055698	-0.084594	18292292.83	237.055705	-0.053135	13418415.05
C_19H_11O_3-	287.071588	0.768552	16661977.05	287.071355	-0.044337	31409105.04	287.071458	0.31443	7574136.72	287.071462	0.329639	6904281.1
Inorganic salts												
NaCl_2-	92.927944	-0.86086	1832671.34	92.927887	-1.469435	536664.72	92.927859	-1.770034	30824829.07	92.927902	-1.312747	65464.48
CuCl-	132.867868	0.099266	974714.12	132.867778	-0.581307	407694.97	132.867883	0.210764	15893844.16	132.867815	-0.30521	110199.04
FeCl_3-	160.842022	-0.1673	19007.93	160.841949	-0.618379	654837.59	160.841937	-0.696757	1375610.61	160.84204	-0.054896	11855.11

(b)

	Injector needle 1			Injector needle 2			Injector needle 3			Injector needle 4		
Formula	Centre Mass (u)	Deviation (ppm)	Area (Intensity)	Centre Mass (u)	Deviation (ppm)	Area (Intensity)	Centre Mass (u)	Deviation (ppm)	Area (Intensity)	Centre Mass (u)	Deviation (ppm)	Area (Intensity)
Linear carboxylic acids												
C_16H_31O_2-	255.233534	2.274657	32392	119.050203	1.447582	1427	255.233142	0.738967	26283.07	255.23324	1.120394	1688051.07
C_18H_35O_2-	283.264786	1.877228	26343	79.957079	0.55141	2210	283.264451	0.694995	32452.69	283.264486	0.817631	1569883
alkyl benzyl sulfonate												
C_8H_7SO_3-	183.012386	1.353485	22192537	183.012139	0.00209	5819556	183.012136	-0.011823	1430864.97	183.012231	0.503664	44010176.65
C_17H_27SO_3-	311.169307	2.147868	1583050	311.16883	0.614004	295070	311.168877	0.764692	95440.35	311.168926	0.923153	2597729.87
C_18H_29SO_3-	325.18481	1.603105	1684842	325.18431	0.06375	275893	325.184338	0.150447	94921.67	325.184439	0.461729	2493037.29
Alkyl salicylate												
C_7H_5O_3-	137.024452	0.253141	66999	137.024361	-0.416457	49711	137.024348	-0.5071	23777.63	137.024397	-0.149005	262706.6
C_8H_7O_3-	151.040154	0.573618	30294	151.040014	-0.356927	13662	151.039979	-0.586557	5957.47	151.040083	0.101392	119569.78
C_9H_9O_3-	165.055861	0.865653	5359	**x**	**x**	**x**	**x**	**x**	**x**	165.055687	-0.185419	21534.68
C_10H_11O_3-	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	179.071536	0.940997	5449.47
C_11H_13O_3-	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**
Fused salicylate												
C_11H_7O_3-	187.040136	0.363198	147936.98	187.04006	-0.040527	115834	187.040091	0.12669	72968.62	187.040078	0.053729	1022747.02
C_15H_9O_3-	237.056015	1.253406	28430.83	237.055871	0.646441	31860	237.055988	1.138332	5266	237.055876	0.667145	203301.73
C_19H_11O_3-	287.072042	2.350046	24136.44	287.071727	1.251244	12624	287.071536	0.586644	5490.39	287.071666	1.039181	212776.18
Inorganic salts												
NaCl_2-	**x**	**x**	**x**	92.927933	-0.979267	12669	**x**	**x**	**x**	92.927915	-1.171798	1667331.01
CuCl_2-	132.867997	1.067715	2204821	132.867809	-0.348502	327848	132.867835	-0.154615	339527.04	132.867898	0.319417	20307913.51
FeCl_3-	160.842106	0.357264	286684	160.841993	-0.347658	657101	160.842019	-0.182576	427201.64	160.842082	0.206867	8520590.69

	Injector needle 5			Injector needle 6			Injector needle 7			Injector needle 8		
Formula	Centre Mass (u)	Deviation (ppm)	Area (Intensity)	Centre Mass (u)	Deviation (ppm)	Area (Intensity)	Centre Mass (u)	Deviation (ppm)	Area (Intensity)	Centre Mass (u)	Deviation (ppm)	Area (Intensity)
Linear carboxylic acids												
C_16H_31O_2-	119.050203	1.447582	1427	255.233208	0.994485	21970.59	255.233422	1.833339	2835332.13	255.233252	1.170195	3879830.75
C_18H_35O_2-	79.957079	0.55141	2210	283.264482	0.80433	12433.23	283.264685	1.520272	2873077.9	283.264505	0.886701	3987783.12
alkyl benzyl sulfonate												
C_8H_7SO_3-	183.012139	0.00209	5819556	183.012142	0.02027	4578121.59	183.012252	0.618415	85145793.81	183.012119	-0.106631	93708486.39
C_17H_27SO_3-	311.16883	0.614004	295070	311.168798	0.50959	259537.35	311.169219	1.865243	8927499.02	311.168997	1.149114	10068750.28
C_18H_29SO_3-	325.18431	0.06375	275893	325.184274	-0.045777	241332.47	325.184756	1.435994	8625199.93	325.184524	0.721693	10023950.19
Alkyl salicylate												
C_7H_5O_3-	137.024361	-0.416457	49711	137.024354	-0.467618	26262.31	137.024393	-0.178848	85505.23	137.024341	-0.559588	8463.23
C_8H_7O_3-	151.040014	-0.356927	13662	151.040027	-0.266522	9760.36	151.040141	0.488705	5252.86	**x**	**x**	**x**
C_9H_9O_3-	165.055727	0.056165	2044	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**
C_10H_11O_3-	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**
C_11H_13O_3-	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**	**x**
Fused salicylate												
C_11H_7O_3-	187.04006	-0.040527	115834	187.040039	-0.152058	72097.98	187.03986	-1.1127	9859.57	187.03992	-0.787472	3877.94
C_15H_9O_3-	237.055871	0.646441	31860	237.055825	0.4508	12700.64	237.05586	0.600935	8653.92	237.055703	-0.060512	3247.7
C_19H_11O_3-	287.071727	1.251244	12624	**x**	**x**	**x**	287.074033	9.2849	10854.44	287.074189	9.827158	17419.53
Inorganic salts												
NaCl_2-	92.927933	-0.979267	12669	92.927862	-1.742616	3816520.31	92.927906	-1.264266	697180.81	92.927893	-1.410817	140822.78
CuCl_2-	132.867809	-0.348502	327848	132.867827	-0.214709	1837499.93	132.867953	0.739501	2901434.06	132.867787	-0.513206	260626.41
FeCl_3-	160.841993	-0.347658	657101	160.84202	-0.179157	5641960.92	160.842011	-0.237538	103094.27	**x**	**x**	**x**

Table S5: 3D OrbiSIMS accurate mass ion table for a selection of PAHs manually identified in **(a)** injector tip deposits **i.** injector tips 1-4, **ii.** Injector tips 5-8. **(b)** Deposits from injector needles **i.** injector tips 1-4, **ii.** Injector tips 5-8. All ion peak tables were exported from Surface Lab software (IONTOF GmbH, version 7.1.b). Deviation (ppm) refers to the difference between the observed and expected ion mass. The observed mass is measured as the center mass of the ion peak.

(a) i.

	Injector tip 1			Injector tip 2			Injector tip 3			Injector tip 4		
Formula	**Center Mass (u)**	**Deviation (ppm)**	**Area (intensity)**	**Center Mass (u)**	**Deviation (ppm)**	**Area (intensity)**	**Center Mass (u)**	**Deviation (ppm)**	**Area (intensity)**	**Center Mass (u)**	**Deviation (ppm)**	**Area (intensity)**
C_7H_7+	91.054391	1.803584	220248460.8	91.054417	2.092466	1688466270	91.054481	2.79573	680990858.6	91.054452	2.473783	2060640240
C_9H_7+	115.054227	0.000425	264994336.1	115.054235	0.076433	2671248376	115.054302	0.65455	481265460.1	115.054227	0.003842	2911749255
C_10H_8+	128.062054	0.017629	191543903.4	128.062012	-0.308323	1587896933	128.062041	-0.085723	353653717.6	128.061963	-0.69352	1535026175
C_11H_7+	139.054282	0.396924	55000463.42	139.05419	-0.260142	623939207.4	139.054194	-0.232484	124562511.6	139.05409	-0.983115	513424322.9
C_11H_9+	141.069913	0.253898	65774547.74	141.069816	-0.432129	586445049.9	141.069808	-0.485367	112755911.6	141.069717	-1.13554	527778865.7
C_12H_6+	150.046465	0.422541	31340871	150.046372	-0.196337	505157693.4	150.046384	-0.116456	104486745.9	150.04626	-0.946871	399261801.7
C_12H_8+	152.062114	0.408928	113574249.7	152.062013	-0.255315	1384768718	152.062026	-0.170764	249410086.8	152.061906	-0.960141	1096427815
C_13H_10+	166.077746	0.268938	4017204.32	166.07761	-0.551346	42290992.91	166.07759	-0.672667	7792591.18	166.077533	-1.015587	32486735.42
C_14H_8+	176.06212	0.389718	28107938.92	176.062031	-0.117553	478926799.9	176.062041	-0.058784	90913536.11	176.061897	-0.877556	338591407.8
C_14H_10+	178.077762	0.340157	32863797.52	178.077669	-0.186154	517217800.8	178.077664	-0.210667	91531335.35	178.077536	-0.932558	383419333.1
C_15H_10+	190.077764	0.327878	5163717.52	190.077615	-0.454913	85913043.55	190.077541	-0.847861	13133460.62	190.077523	-0.940806	70446656.07
C_16H_10+	202.077805	0.509798	39654177.03	202.077699	-0.015732	662653320.5	202.07769	-0.057531	121381964.2	202.077547	-0.767199	520942328.9
C_17H_9+	213.069885	0.040996	20938074.46	213.069875	-0.007109	368564736	213.069942	0.307054	71759257.86	213.069791	-0.40305	282481375.4
C_17H_12+	216.09327	-0.376328	1057136.32	216.093314	-0.175679	14844662.97	216.093396	0.206441	2828815.04	216.093385	0.154943	14480617.56
C_18H_10+	226.077611	-0.399706	25830389.84	226.077696	-0.026091	469273992.9	226.077855	0.677506	82336582.99	226.077678	-0.102933	345454275.1
C_18H_12+	228.093254	-0.427101	5405813.56	228.093287	-0.283097	77185699.57	228.093343	-0.038075	12765687.31	228.093334	-0.076095	75772286.45
C_19H_11+	239.085412	-0.48178	21659776.36	239.085501	-0.106089	379258842.4	239.08562	0.388567	59134767.88	239.085483	-0.182817	276958371.1
C_20H_10+	250.077588	-0.456598	15698956.32	250.077671	-0.12362	295830313.1	250.07779	0.351657	50162800.61	250.077649	-0.212215	210718873.1
C_20H_12+	252.09323	-0.483495	11625833.55	252.093299	-0.211116	193311549.7	252.093365	0.050868	28880456.22	252.093295	-0.2238	149439774.3
C_21H_11+	263.085425	-0.388063	16217857.96	263.085516	-0.042452	299889979.4	263.08563	0.390543	45629264.92	263.085499	-0.104591	205369941.8
C_21H_13+	265.101094	-0.311131	4427366.56	265.101129	-0.180566	75335344.4	265.101203	0.097048	10753232.52	265.101165	-0.044997	53652078.18
C_22H_12+	276.09327	-0.297847	12279667.64	276.093351	-0.004242	224419161.1	276.093448	0.347041	32871673.44	276.093347	-0.018182	155035369.6
C_22H_13+	277.101106	-0.254852	1504207.16	277.101147	-0.10745	28805716.72	277.101266	0.322414	4368354.62	277.101186	0.033475	15500463.82
C_22H_14+	278.108925	-0.275	509231.14	278.108961	-0.146095	9860535.29	278.109101	0.355281	2062768.54	278.109017	0.056135	4902314.65

C_23H_13+	289.101074	-0.356261	7243789.37	289.101136	-0.139728	131472811.3	289.101225	0.167471	18263229.42	287.085481	-0.159803	136092035.3
C_24H_12+	300.093263	-0.296302	10108302.67	300.093348	-0.013013	194826587.9	300.09345	0.32765	29293136.06	300.093325	-0.09056	132710367
C_25H_13+	313.101063	-0.365151	8015296.98	313.101132	-0.144102	151806745.9	313.101236	0.188085	21760579.55	313.101097	-0.256354	102942215.1
C_28H_14+	350.10891	-0.26334	4259903.17	350.108986	-0.046172	84904202.31	350.109172	0.484767	13780740.34	350.108944	-0.16661	58778231.64
C_30H_14+	374.108887	-0.306656	3597497.03	374.108985	-0.043883	74873512.38	374.109205	0.543553	13399136.28	374.108938	-0.170996	51386140.88
C_31H_15+	387.116719	-0.279998	2477593.21	387.116805	-0.056591	51458629.42	387.11703	0.525071	9785221.46	387.116749	-0.200088	34944255.36
C_32H_14+	398.108878	-0.312269	2641992.08	398.109004	0.006091	57438287.82	398.109249	0.619819	11626574.96	398.108949	-0.133665	39473599.56
C_34H_16+	424.12454	-0.264376	1087448.21	424.12465	-0.005062	25009825.52	424.124925	0.644423	6367120.12	424.124574	-0.1847	15994521.82
C_36H_18+	450.14026	-0.094399	128990.8	450.140373	0.15853	4165924.76	450.14078	1.061213	1794847.12	450.140244	-0.128952	1867108.07
C_40H_10+	490.07773	0.057351	46938.28	490.077789	0.178336	2422968.76	490.07828	1.179391	1729546.04	490.077654	-0.097153	754829.58
C_40H_16+	496.124577	-0.151049	492886.13	496.12473	0.158034	13918251.76	496.125206	1.116745	5034944.31	496.124598	-0.109689	7523590.3
C_40H_18+	498.140288	-0.028221	195151.52	498.140401	0.198034	6121946.57	498.140868	1.136672	2743033.86	498.140249	-0.106578	2984368.84
C_42H_16+	520.124591	-0.116461	281452.24	520.124774	0.23409	9660272.38	520.125305	1.254704	4249984.64	520.124632	-0.037548	4997282.98
C_42H_18+	522.140263	-0.074126	184985.21	522.140427	0.239649	5905570.22	522.140987	1.31266	2876498.39	522.140286	-0.030681	2876519.89
C_46H_20+	572.155742	-0.366705	35810.07	572.155992	0.069164	1417866.96	572.156644	1.209089	1164152.94	572.155835	-0.205423	655321.62
C_49H_21+	609.163533	-0.40033	27343.82	609.163785	0.013407	803178.97	609.164505	1.194545	753367.24	609.163656	-0.199075	386861.06
C_52H_22+	646.1718	0.306888	11905.84	646.171516	-0.132575	384985.01	646.172336	1.135587	389211.44	646.171392	-0.324515	222833.16
C_54H_22+	670.171874	0.40496	8172.84	670.171657	0.082133	337742.43	670.172363	1.135747	406085.88	670.171535	-0.099958	196045.3
C_60H_22+	742.171626	0.031837	8933.26	742.171709	0.144038	216199.94	742.172483	1.186508	303925.62	742.171551	-0.068581	131816.75
C_62H_22+	766.168875	-3.559309	13624.09	766.170327	-1.664216	286349.07	766.171881	0.363601	286907.57	766.170472	-1.474839	167655.43
C_66H_20+	812.155857	-0.117511	6648.86	812.155296	-0.807252	174863.42	812.156783	1.022671	169566.58	812.155073	-1.082687	110667.08
C_80H_22+	**x**	**x**	**x**	**x**	**x**	**x**	982.169805	-1.830246	21981.16	982.168633	-3.023176	59581.5

ii.

	Injector tip 5			Injector tip 6			Injector tip 7			Injector tip 8		
Formula	Center Mass (u)	Deviation (ppm)	Area (intensity)	Center Mass (u)	Deviation (ppm)	Area (intensity)	Center Mass (u)	Deviation (ppm)	Area (intensity)	Center Mass (u)	Deviation (ppm)	Area (intensity)
C_7H_7+	91.054378	1.665768	2519091033	91.055613	1.325198	195146624.4	91.054401	1.919228	262648770.9	91.054392	1.816091	3605472890
C_9H_7+	115.054158	-0.592953	2698071741	115.055754	-0.780821	198111469.6	115.054179	-0.415317	546745763.7	115.054172	-0.476754	3883322076
C_10H_8+	128.061878	-1.357532	1632267769	128.063613	-1.733088	136164450.4	128.061913	-1.085077	279432184.7	128.061894	-1.231983	2205441645
C_11H_7+	139.053993	-1.680742	577418249.4	139.0559	-2.11091	52664446.13	139.054037	-1.365939	102500279.2	139.054028	-1.428099	752710393.8
C_11H_9+	141.069609	-1.894562	468225857.7	141.071508	-2.329546	47505843.47	141.069662	-1.522097	98588972.18	141.069643	-1.653963	810299129.8
C_12H_6+	150.046156	-1.634965	503766064.8	150.048901	-2.090925	28374388.67	150.046201	-1.333922	97923238.8	150.046198	-1.360288	690098208.6
C_12H_8+	152.061799	-1.661396	1052351121	152.064616	-1.898514	87514535.17	152.061848	-1.339913	327177251.3	152.06184	-1.391724	1844808883
C_13H_10+	166.077384	-1.912228	29620142.45	166.078812	-2.100303	3379524.91	166.077399	-1.825465	10999315.53	166.077387	-1.895508	76262623.35
C_14H_8+	176.06176	-1.655941	338745009.8	176.065384	-2.127207	30453188.52	176.061847	-1.16213	120029979.3	176.061833	-1.239935	676163344.7
C_14H_10+	178.077394	-1.729909	313627250.3	178.079262	-2.049098	38552000.24	178.077482	-1.234279	126187417.7	178.077467	-1.316605	826412272.2
C_15H_10+	190.077343	-1.88665	52274227.13	190.079136	-2.894279	5606906.5	190.077377	-1.70758	25680972.4	190.077344	-1.882091	159876313.7
C_16H_10+	202.077382	-1.583697	472579165.8	202.07941	-2.019224	44580838.61	202.077486	-1.067523	211692051.1	202.077468	-1.156988	1159567296
C_17H_9+	213.069605	-1.274248	300352330.3	213.072671	-1.854997	18403650.94	213.069722	-0.725332	106404447.1	213.06971	-0.781283	603873904.6
C_17H_12+	216.093164	-0.870285	12571129.96	216.096182	-1.984568	1618091.22	216.093208	-0.667104	8545442.71	216.093159	-0.890938	47475048.02
C_18H_10+	226.077492	-0.926711	316371030.1	226.081059	-1.236709	18615642.91	226.07762	-0.362435	156540611.6	226.077608	-0.416354	768057334.1
C_18H_12+	228.093111	-1.054395	63287409.17	228.095193	-1.631755	4201532.44	228.093162	-0.833435	30537896.56	228.093118	-1.024119	177680303.6
C_19H_11+	239.085273	-1.059842	246985918.6	239.088059	-1.840824	14275628.2	239.085408	-0.498633	128608038.2	239.085372	-0.645398	581878015
C_20H_10+	250.077435	-1.065285	209353472.7	250.079933	-1.871107	8262272.3	250.077545	-0.628144	82695760.44	250.077509	-0.77139	432225470
C_20H_12+	252.09307	-1.116495	127426798.1	252.095452	-2.048458	6732121.75	252.093163	-0.747584	59504988	252.093107	-0.970073	286924041.8
C_21H_11+	263.085273	-0.963699	193152191.7	263.08784	-1.823974	7836917.02	263.085393	-0.507428	88828276.58	263.085349	-0.675983	416673527.4
C_21H_13+	265.100932	-0.922587	45710343.61	265.103653	-1.700594	2289855.48	265.100967	-0.79106	25475542.66	265.100926	-0.946606	116333686.6
C_22H_12+	276.093117	-0.85194	139350785.2	276.095753	-1.602453	5555215.76	276.093214	-0.500631	64565967.96	276.093167	-0.670542	304815203.9
C_22H_13+	277.100954	-0.803947	14010164.71	277.103592	-1.423508	687781.82	277.100958	-0.791229	9651024.54	277.100975	-0.727809	44452820.51
C_22H_14+	278.10878	-0.796409	5643422.32	278.111661	-1.594163	480500.04	278.108817	-0.664088	4817813.38	278.108779	-0.80171	22001916.78
C_23H_13+	287.085245	-0.982947	143008777	287.088053	-1.730315	4208630.12	287.085321	-0.715267	48977377.39	287.085292	-0.81755	277851740.3
C_24H_12+	300.093089	-0.874758	128231848.2	300.096251	-1.561978	3727457.1	300.093154	-0.660241	51367469.03	300.093125	-0.754712	264826232.1
C_25H_13+	313.100862	-1.004977	96715352.09	313.103786	-1.467476	2655324.47	313.100911	-0.848388	42440546.42	313.100891	-0.913288	204888569.2

C_28H_14+	350.108704	-0.849385	59928190.96	350.112271	-0.852717	1286982.26	350.108735	-0.761425	23446746.22	350.108757	-0.699919	126069259.4
C_30H_14+	374.108676	-0.870206	58887821.76	374.112857	-0.864883	964401.44	374.108722	-0.749105	19705056.87	374.108756	-0.657828	119155502.2
C_31H_15+	387.116504	-0.833766	41035088.04	387.120765	-0.56942	636111.17	387.116525	-0.779168	15712273.01	387.116577	-0.646708	88383692.77
C_32H_14+	398.108668	-0.837702	52580334.03	398.11324	-0.534482	623134.23	398.108728	-0.686875	14907027.19	398.108773	-0.57541	102930938.3
C_34H_16+	424.124296	-0.84034	24404654.95	424.131182	-0.320692	254578.88	424.124346	-0.72048	8881133.02	424.124399	-0.595631	56168308.05
C_36H_18+	450.139999	-0.673295	3592425.98	450.146314	-0.045063	47227.05	450.140097	-0.45513	2493675.89	450.140166	-0.303017	13884671.76
C_40H_10+	490.077342	-0.733679	9757347.9	490.083052	0.064426	11005.33	490.077434	-0.545971	445438.69	490.077536	-0.338533	17151515
C_40H_16+	496.124303	-0.702819	20385786.25	496.130392	0.374045	89438.04	496.1244	-0.508638	4678790.73	496.124499	-0.30924	44434175.7
C_40H_18+	498.139983	-0.641168	7359834.48	498.146156	0.474814	64622.8	498.140078	-0.449847	3042856.36	498.140188	-0.228189	22609913.97
C_42H_16+	520.124318	-0.64183	17238631.12	520.130313	0.121766	51327.11	520.12442	-0.446627	3349713.41	520.124554	-0.188727	37587701.47
C_42H_18+	522.139991	-0.595122	8278585.93	522.145884	0.289244	49886.09	522.140114	-0.360761	2793213.88	522.140233	-0.131288	23914717.28
C_46H_20+	572.155575	-0.658543	1968437.88	572.162095	-1.068799	17812.21	572.155714	-0.416932	984313.77	572.155867	-0.149394	8052819.67
C_49H_21+	609.163322	-0.747002	1201892.65	609.170948	1.48598	10525.98	609.163501	-0.452838	655401.91	609.163665	-0.183319	5384772.86
C_52H_22+	646.171073	-0.819222	602624.36	646.178463	-0.897059	9687.84	646.171166	-0.675656	308519.61	646.171406	-0.304107	2723504.91
C_54H_22+	670.17111	-0.734879	646615.87	670.179833	-0.559566	4955.31	670.171195	-0.607273	344240.8	670.171443	-0.237347	2946489.58
C_60H_22+	742.171004	-0.806497	597373.24	742.17951	1.2439	454.79	742.171219	-0.516149	190333.66	742.171441	-0.217442	2581448.82
C_62H_22+	766.170283	-1.721811	659534.12	766.187631	-0.469373	1184.41	766.170699	-1.178938	175158.88	766.170925	-0.883742	2496503.02
C_66H_20+	812.154988	-1.18707	557076.32	**x**	**x**	**x**	812.155316	-0.783691	69317.29	812.155543	-0.503374	1752231.43
C_80H_22+	982.1703	-1.3402	88021	**x**	**x**	**x**	982.170143	-1.486115	22370.9	982.16904	-2.608936	287088.25

(b) i.

	Injector needle 1			Injector needle 2			Injector needle 3			Injector needle 4		
Formula	Center Mass (u)	Deviation (ppm)	Area (intensity)	Center Mass (u)	Deviation (ppm)	Area (intensity)	Center Mass (u)	Deviation (ppm)	Area (intensity)	Center Mass (u)	Deviation (ppm)	Area (intensity)
C_7H_7+	91.054442	2.36962	10795.52	91.05446	2.567513	2487062.32	91.054474	2.720858	8900815.18	91.054426	2.187108	2753536.42
C_9H_7+	115.054233	0.051761	81638.75	115.054267	0.35057	4070307.73	115.054272	0.394698	23371405.35	115.05422	-0.057023	5256106.67
C_10H_8+	128.061973	-0.616866	42735.47	128.062002	-0.390263	2369330.81	128.062007	-0.345617	12022456.55	128.061944	-0.842741	3201968.46
C_11H_7+	139.054078	-1.071567	12319.76	139.054124	-0.741279	893598.47	139.054133	-0.675542	2648937.8	139.054062	-1.183246	1114582.08
C_11H_9+				141.069744	-0.942825	735626.36	141.06976	-0.825352	3686255.77	141.069684	-1.364855	958071.86
C_12H_6+				150.046292	-0.733505	746654.73	150.046311	-0.602751	2034093.29	150.046232	-1.133459	611952.75
C_12H_8+				152.061929	-0.805109	1964987.66	152.061959	-0.608235	8152101.92	152.061868	-1.208676	1925381.66
C_13H_10+				166.077492	-1.260469	53684.9	166.077536	-0.995255	388911.21	166.077453	-1.497085	38107.99
C_14H_8+				176.061919	-0.750987	559120.07	176.061969	-0.468863	2555733.46	176.061858	-1.099376	514380.51
C_14H_10+				178.077559	-0.79943	644913.34	178.077613	-0.500801	3241625.46	178.077495	-1.159113	656872.07
C_15H_10+				190.077521	-0.949856	99159.82	190.077537	-0.86471	688258.16	190.07744	-1.377907	89528.9
C_16H_10+				202.07755	-0.750198	714654.85	202.077635	-0.331052	5349477.51	202.077496	-1.019208	826564.73
C_17H_9+				213.069817	-0.281822	375038.06	213.069878	0.005138	2221680.22	213.069756	-0.564598	430336.61
C_17H_12+				216.093419	0.309181	11269.27	216.093403	0.235761	281288.34	216.093264	-0.404041	14140.2
C_18H_10+				226.077693	-0.038272	392783.06	226.077783	0.360531	3404985.41	226.07764	-0.275038	463741.6
C_18H_12+				228.093369	0.0749	73860.44	228.093348	-0.016496	755955.5	228.093271	-0.356224	102264.68
C_19H_11+				239.085494	-0.1387	296869.73	239.08558	0.220704	2997585.06	239.085438	-0.370387	386630.79
C_20H_10+				250.077677	-0.098953	206749.3	250.077729	0.10843	1607670.27	250.077629	-0.289352	242896.01
C_20H_12+				252.093302	-0.196721	138313.11	252.093365	0.054202	1422720.13	252.093284	-0.27085	179907.56
C_21H_11+				263.085549	0.083363	185859.92	263.085594	0.254341	1890089.44	263.085466	-0.231246	235375.2
C_21H_13+				265.101212	0.132138	46951.48	265.101207	0.112235	637186.68	265.101109	-0.256957	60209.56
C_22H_12+				276.093395	0.157916	121893.5	276.093428	0.274921	1404540.75	276.093341	-0.038612	160799.08
C_22H_13+				277.101252	0.273044	10305.16	277.101228	0.186392	273390.96	277.101044	-0.480459	9235.13
C_22H_14+				278.108996	-0.022743	4136.82	278.109087	0.307702	123027.71	278.108859	-0.514162	6699.09
C_23H_13+				289.101174	0.042435	66577.76	287.085556	0.101604	958929.48	287.085484	-0.147571	131662.16
C_24H_12+				300.093349	-0.008866	87711.33	300.093412	0.201669	1068440.5	300.093329	-0.076425	102718.69
C_25H_13+				313.10117	-0.020713	59954.72	313.101193	0.051772	944141	313.101078	-0.315146	78540.63

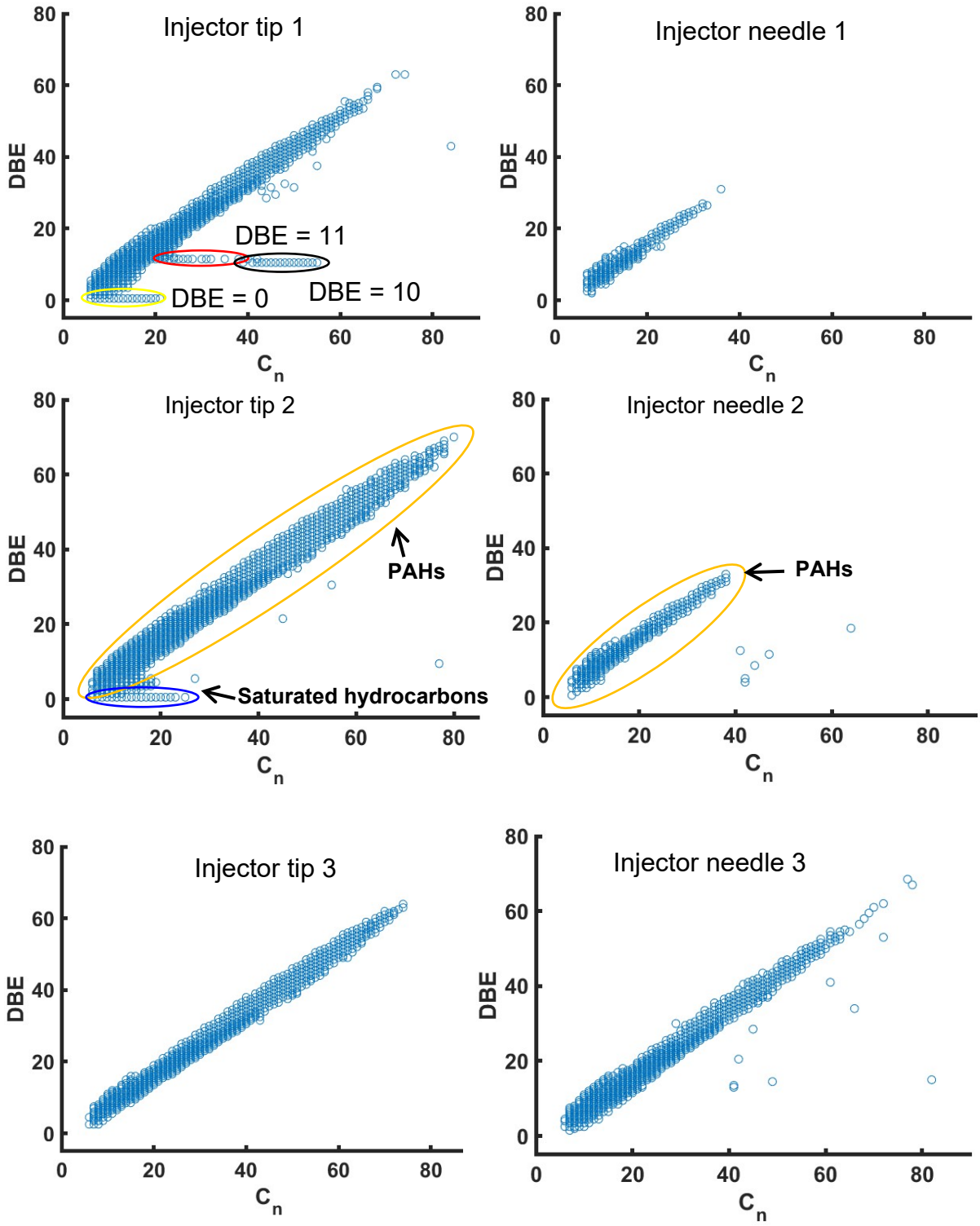
C_28H_14+		350.10901	0.024645	22395.56	350.109048	0.132216	499448.63	350.108944	-0.164713	26967.89
C_30H_14+		374.109015	0.034357	21020.63	374.109037	0.093319	377793.25	374.108933	-0.184251	12541.58
C_31H_15+		387.117001	0.450215	11137.93	387.116841	0.035719	320463.9	387.116795	-0.081329	7701.38
C_32H_14+		398.10912	0.296831	12184.16	398.109077	0.189256	260855.39	398.108906	-0.240462	11622.62
C_34H_16+					424.124709	0.133657	165581.84	424.124685	0.078784	4369.54
C_36H_18+					450.140444	0.314601	38668.45			
C_40H_10+					490.077995	0.597615	547.14			
C_40H_16+					496.124726	0.149499	51100.27			
C_40H_18+					498.140596	0.591081	32116.4			
C_42H_16+					520.124716	0.12295	24890.5			
C_42H_18+					522.140347	0.086731	34349.63			
C_46H_20+					572.156197	0.428248	6460.84			

ii.

Formula	Injector needle 5			Injector needle 6			Injector needle 7			Injector needle 8		
C_7H_7+	Center Mass (u)	Deviation (ppm)	Area (intensity)	Center Mass (u)	Deviation (ppm)	Area (intensity)	Center Mass (u)	Deviation (ppm)	Area (intensity)	Center Mass (u)	Deviation (ppm)	Area (intensity)
C_9H_7+	91.054429	2.217383	48917767.81	91.053336	2.173303	2385472.48	91.053336	2.173303	2385472.48	91.054414	2.058531	2073659.82
C_10H_8+	115.054223	-0.027953	72336337.31	115.052851	-0.065253	5607633.77	115.052851	-0.065253	5607633.77	115.054202	-0.212122	3727549.35
C_11H_7+	128.061953	-0.771347	44650777.51	128.060691	-0.817399	3402542.25	128.060691	-0.817399	3402542.25	128.061941	-0.866345	2165602.59
C_11H_9+	139.054065	-1.16508	9248577.96	139.052374	-1.179581	1153835.83	139.052374	-1.179581	1153835.83	139.054042	-1.327213	882600.66
C_12H_6+	141.069693	-1.30117	12980909.03	141.068355	-1.35092	1091975.2	141.068355	-1.35092	1091975.2	141.069653	-1.586892	750449.41
C_12H_8+	150.046232	-1.13022	5705294.61	150.044949	-1.127418	979656.23	150.044949	-1.127418	979656.23	150.046151	-1.667082	489216.28
C_13H_10+	152.061869	-1.200424	17242455.6	152.059701	-1.204068	2776259.93	152.059701	-1.204068	2776259.93	152.061833	-1.438311	1810167.74
C_14H_8+	166.077475	-1.365104	589765.99	166.076799	-1.44059	71826.7	166.076799	-1.44059	71826.7	166.07745	-1.51397	38606.42
C_14H_10+	176.061848	-1.159092	4984750.52	176.059575	-1.100357	817814.19	176.059575	-1.100357	817814.19	176.061828	-1.27102	450314.9
C_15H_10+	178.077485	-1.218599	6482070.29	178.076866	-1.176204	974862.57	178.076866	-1.176204	974862.57	178.077493	-1.172197	704143.21
C_16H_10+	190.077457	-1.285667	1243810.68	190.076671	-1.372013	154164.3	190.076671	-1.372013	154164.3	190.077345	-1.875594	131513.85
C_17H_9+	202.077492	-1.036787	9541383.74	202.076707	-1.045905	1260511.87	202.076707	-1.045905	1260511.87	202.077496	-1.016327	877613.9
C_17H_12+	213.069742	-0.633433	4828923.66	213.067445	-0.610196	612504.02	213.067445	-0.610196	612504.02	213.069673	-0.955733	329605.95
C_18H_10+	216.093334	-0.08201	407474.73	216.092126	-0.165106	23779.12	216.092126	-0.165106	23779.12	216.093079	-1.26306	16727.51
C_18H_12+	226.077643	-0.262022	5547389.76	226.075119	-0.270591	755109.62	226.075119	-0.270591	755109.62	226.077555	-0.650352	414271.76
C_19H_11+	228.09327	-0.358528	1858708.87	228.091952	-0.388635	153725.21	228.091952	-0.388635	153725.21	228.093113	-1.045301	117032.88
C_20H_10+	239.085445	-0.343003	5127481.53	239.083338	-0.384497	586824.51	239.083338	-0.384497	586824.51	239.085354	-0.721052	372164.24
C_20H_12+	250.07762	-0.327695	3093150.35	250.076212	-0.308384	399317.06	250.076212	-0.308384	399317.06	250.077473	-0.913018	175493.83
C_21H_11+	252.093264	-0.349654	2791235.51	252.091686	-0.363972	299323.68	252.091686	-0.363972	299323.68	252.093094	-1.022886	186883.68
C_21H_13+	263.085481	-0.173578	3255689.85	263.083825	-0.243278	379020.56	263.083825	-0.243278	379020.56	263.085307	-0.836001	185885.06
C_22H_12+	265.101119	-0.218555	1060565.12	265.099592	-0.33116	100341.95	265.099592	-0.33116	100341.95	265.100946	-0.87025	66358.81
C_22H_13+	276.093328	-0.086218	2392278.47	276.091745	-0.137451	268370.67	276.091745	-0.137451	268370.67	276.093176	-0.637183	144058.46
C_22H_14+	277.101154	-0.082059	262567.7	277.099562	-0.123638	36466.24	277.099562	-0.123638	36466.24	277.10094	-0.853409	20614.15
C_23H_13+	278.108962	-0.144602	141728.16	278.107298	-0.11711	14994.65	278.107298	-0.11711	14994.65	278.108798	-0.732798	13882.81
C_24H_12+	289.101109	-0.22639	1485867.56	287.083804	-0.24428	213953.71	287.083804	-0.24428	213953.71	287.085326	-0.699453	93245.45
C_25H_13+	300.093317	-0.116511	1898227.42	300.09136	-0.108394	195568.68	300.09136	-0.108394	195568.68	300.093132	-0.734122	79115.36
C_28H_14+	313.101078	-0.315022	1577861.26	313.099318	-0.277459	148029.88	313.099318	-0.277459	148029.88	313.100922	-0.815098	70341.11

C_30H_14+	350.108925	-0.220355	804612.73	350.106988	-0.303351	61979.29	350.106988	-0.303351	61979.29	350.108832	-0.486147	25399.31
C_31H_15+	374.108906	-0.256646	654207.59	374.106535	-0.301773	43086.65	374.106535	-0.301773	43086.65	374.108943	-0.156697	13390.15
C_32H_14+	387.11671	-0.30089	466112.13	387.114622	-0.266519	30586.86	387.114622	-0.266519	30586.86	387.116632	-0.504044	10820.12
C_34H_16+	398.1089	-0.256123	476417.3	398.1063	-0.282261	31175.22	398.1063	-0.282261	31175.22	398.108929	-0.183461	9942.12
C_36H_18+	424.124539	-0.266164	205316.63	424.121789	-0.322677	8195.01	424.121789	-0.322677	8195.01	424.124762	0.260276	3871.22
C_40H_10+	450.140132	-0.378626	33250.2	450.13797	1.167836	339.61	450.13797	1.167836	339.61			
C_40H_16+	490.077629	-0.14851	5419.74	490.074303	-0.004446	704.52	490.074303	-0.004446	704.52			
C_40H_18+	496.124511	-0.283477	96324.92	496.120738	-0.783292	2651.11	496.120738	-0.783292	2651.11			
C_42H_16+	498.140132	-0.340657	37093.8	498.137189	0.202674	724.75	498.137189	0.202674	724.75			
C_42H_18+	520.1246	-0.09996	57554.88	520.120747	-0.884376	1313.03	520.120747	-0.884376	1313.03			
C_46H_20+	522.140169	-0.254016	31503.29									

S6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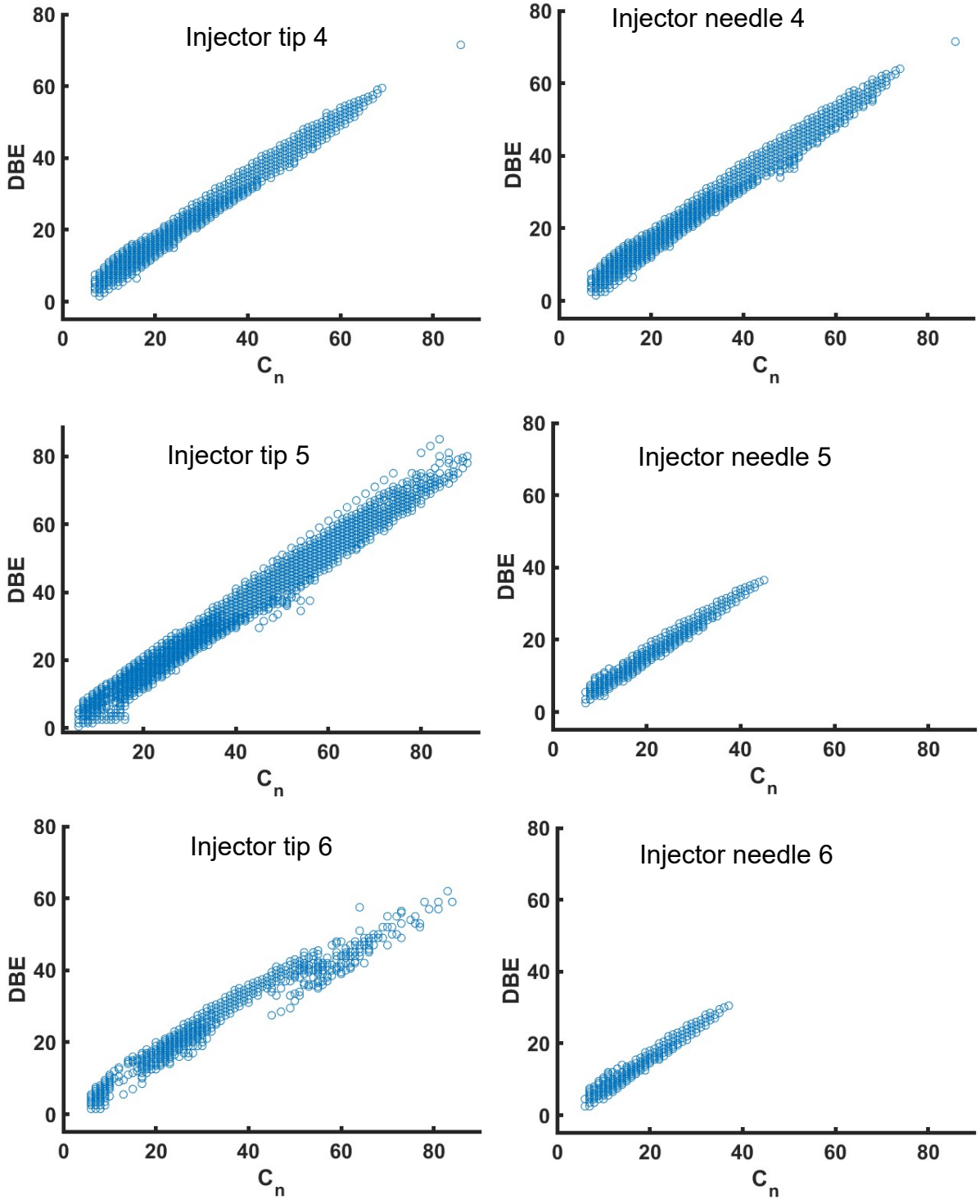
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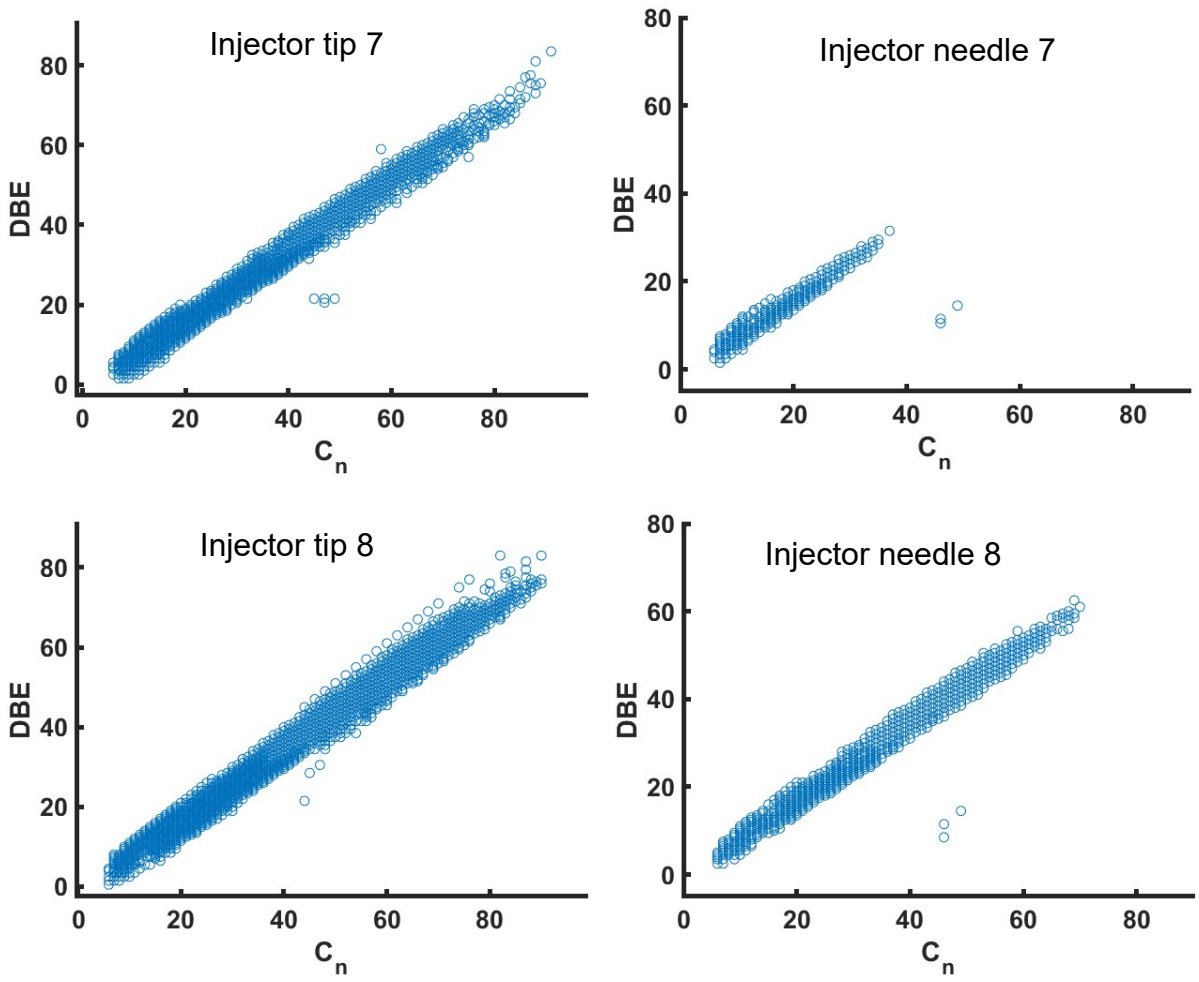
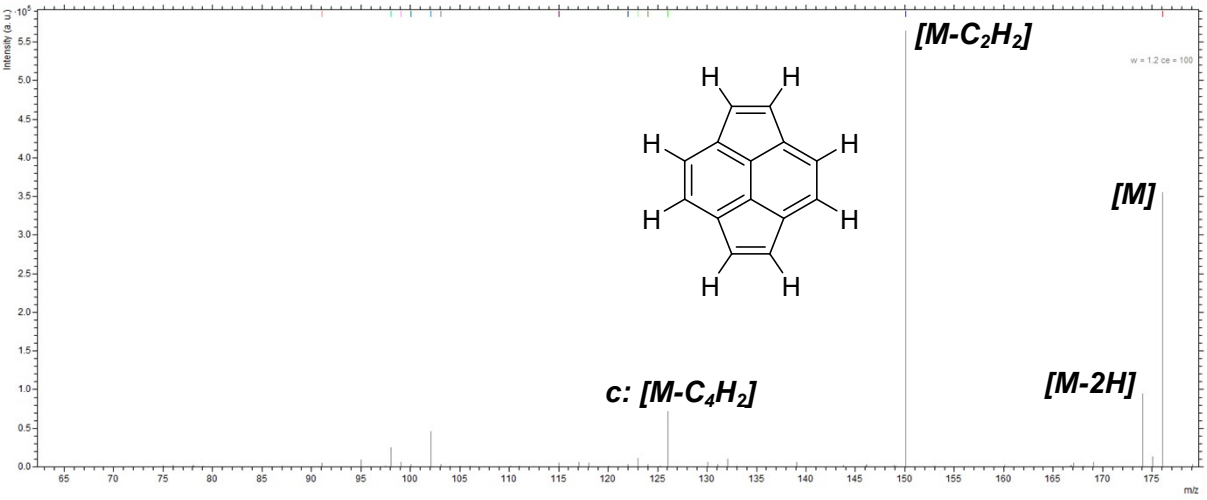


Fig. S6. Double bond equivalence versus C number plot for all CH containing species in deposits.

S7

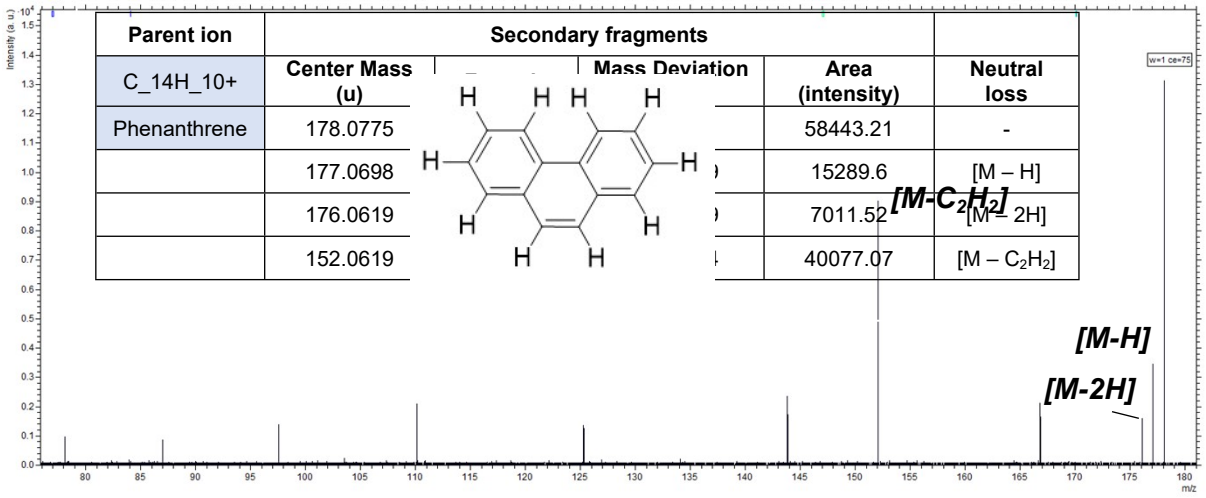
(a)

Parent ion	Secondary fragments				
C_14H_8+	Center Mass (u)	Formula	Mass Deviation (ppm)	Area (intensity)	Neutral loss
	176.061895	C_14H_8+	-0.85552	1456367.92	-
	174.04620	C_14H_6+	-0.9381	415372	[M – 2H]
	150.046251	C_12H_6+	-1.003395	2471493.3	[M – C_2H_2]
	126.046337	C_10H_6+	-0.513255	317449.17	[M – C_4H_2]
	124.030706	C_10H_4+	-0.367688	14827.48	[M – $(C_2H_2)_2$]
	122.015045	C_10H_2+	-0.459973	14826.21	[M – C_4H_6]
	102.046525	C_8H_6+	1.207614	228100.11	[M – $(C_3H)_2$]
	100.030897	C_8H_4+	1.454325	16344.19	[M – $(C_3H_2)_2$]
	98.015273	C_8H_2+	1.747147	123642.9	[M – $(CH)_6$]



(b)

Parent ion	Secondary fragments			
C_14H_10+	Center Mass (u)	Mass Deviation	Area (intensity)	Neutral loss
Phenanthrene	178.0775		58443.21	-
	177.0698		15289.6	[M – H]
	176.0619		7011.52	[M – 2H]
	152.0619		40077.07	[M – C_2H_2]

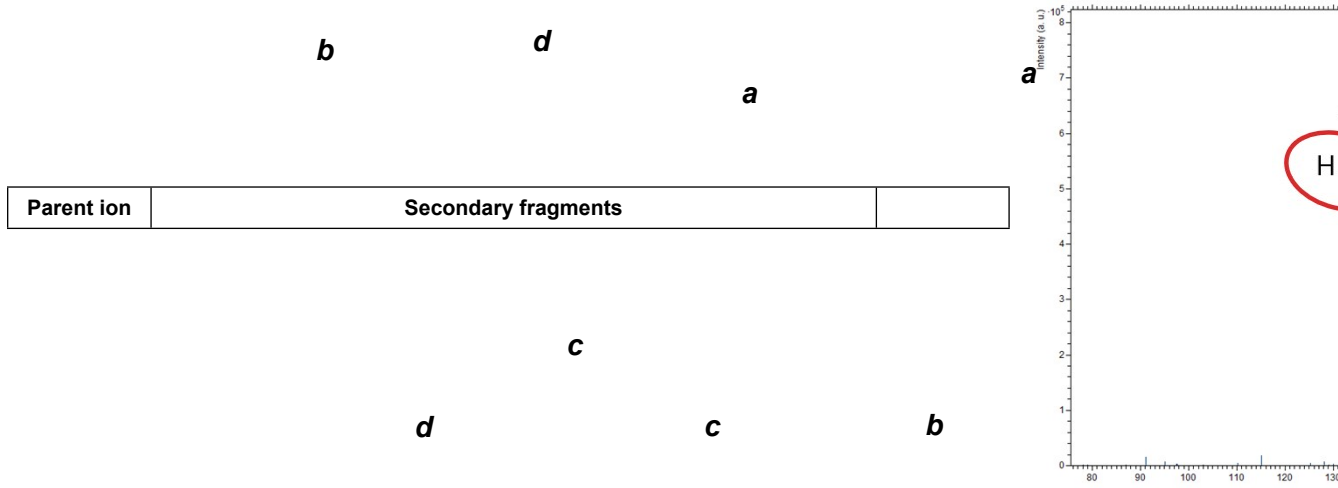


(c)

Parent ion	Secondary fragments				
C_24H_12+	Center Mass (u)	Formula	Mass Deviation (ppm)	Area (intensity)	Neutral Loss

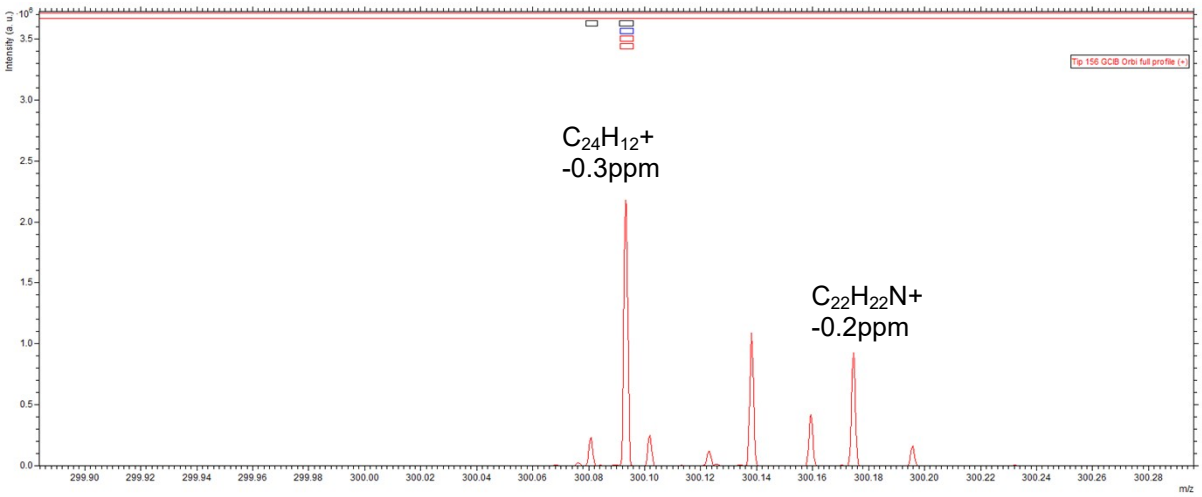
(Coronene)	300.093206	C_24H_12+	-0.486209	1364687	-
	298.077598	C_24H_10+	-0.34793	2971778	[M – 2H]
	274.077588	C_22H_10+	-0.413692	137214.9	[M – C_2H_2]
	228.093164	C_18H_12+	-0.824654	3708.26	[M – C_6]
	226.077673	C_18H_10+	-0.128147	36816.25	[M – C_6H_2]
	178.077454	C_14H_10+	-1.390035	49025.84	[M – $C_{10}H_2$]

i. MS/MS



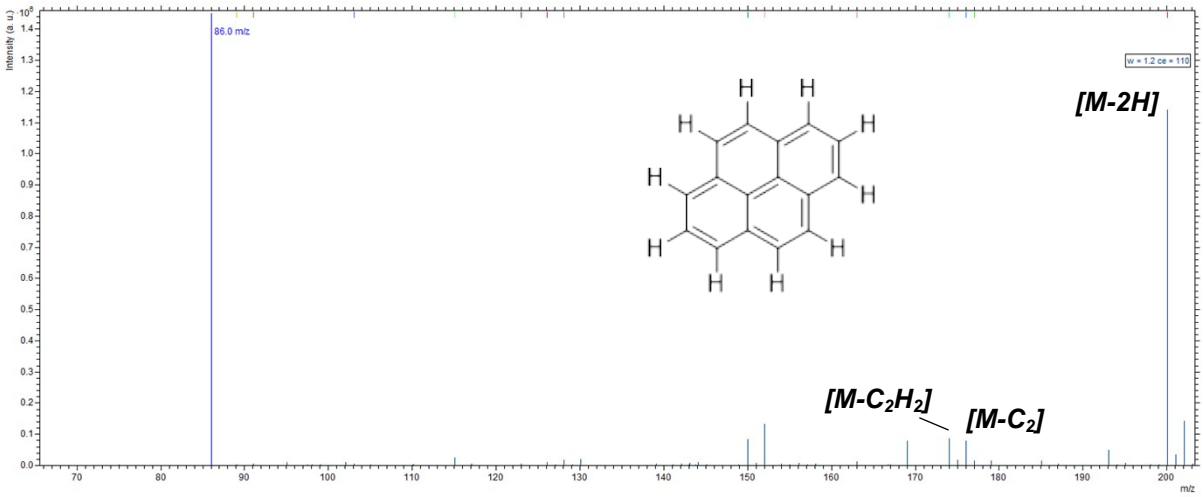
Parent ion	Secondary fragments	

ii. MS1 showing incorporation of C22H22N (0.2 ppm) into the analysis window of MS/MS peaks



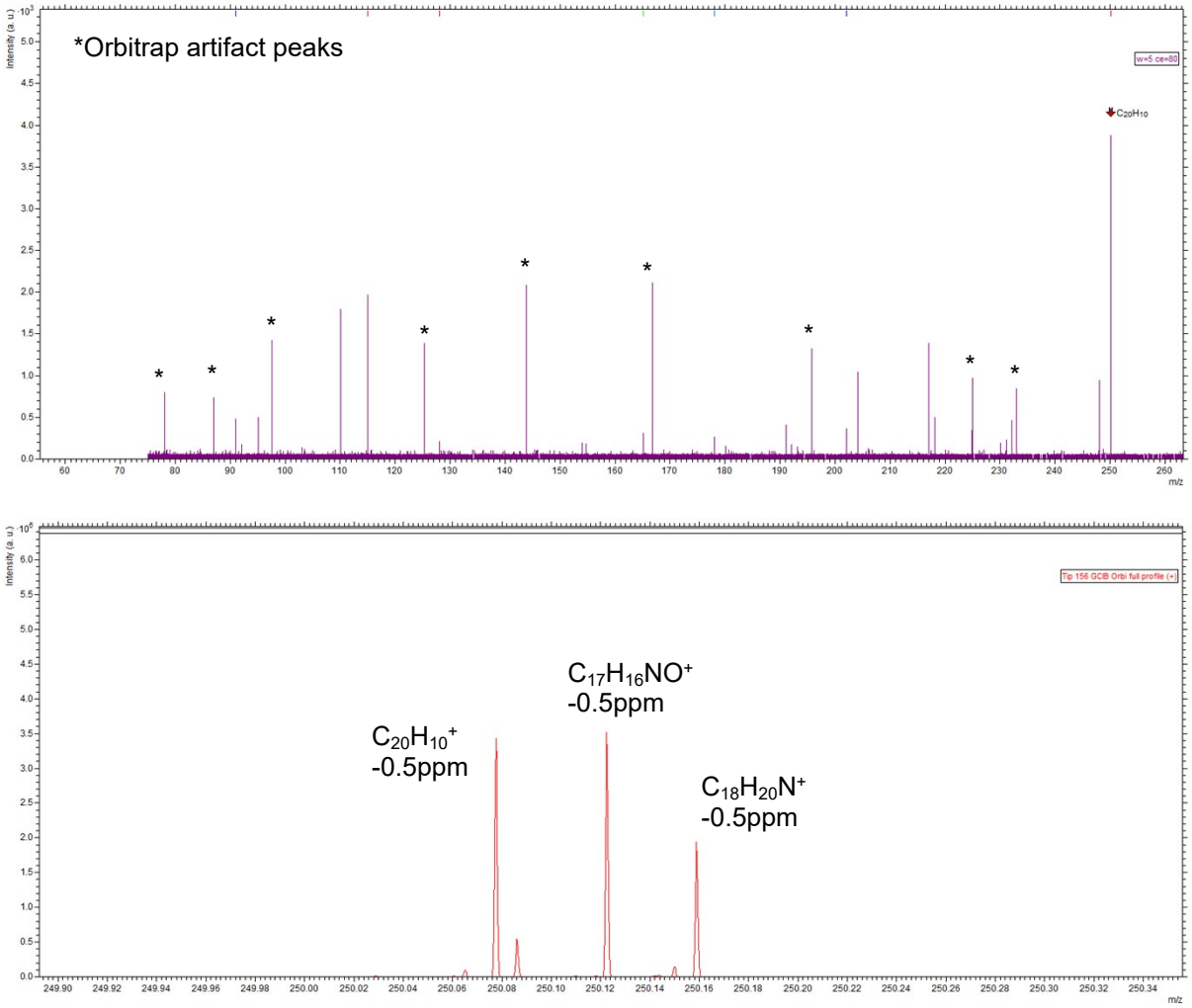
(d)

C_16H_10+	Center Mass (u)	Formula	Mass Deviation (ppm)	Area (intensity)	Neutral Loss
(Pyrene)	200.061899	C_16H_8+	-0.763843	4924050.79	[M – 2H]
	176.061865	C_14H_8+	-1.06155	356336.51	[M – C_2]
	174.046231	C_14H_6+	-0.98235	374845.95	[M – C_2H_2]
	152.06186	C_12H_8+	-1.262254	565560.68	[M – C_4]
	150.046229	C_12H_6+	-1.150128	358354.58	[M – C_4H_2]
	128.061952	C_10H_8+	-0.778506	76947.64	[M – C_6]
	126.046328	C_10H_6+	-0.580416	46241.78	[M – C_6H_2]



(e)

Parent ion	Secondary fragments				
C_20H_10+	Center Mass (u)	Formula	Mass Deviation (ppm)	Area (intensity)	Neutral Loss
(corannulene)	250.077625	C_20H_10+	-0.307937	16490.38	-
	248.0620	C_20H_8+	-0.1411	1478	[M – H_2]
	202.077403	C_16H_10+	-1.476591	1585.07	[M – C_4]
	178.077438	C_14H_10+	-1.48358	1081.03	[M – C_6]
	128.061943	C_10H_8+	-0.850891	834.67	[M – $C_{10}H_2$]
	115.054196	C_9H_7+	-0.262497	9798	[M – $C_{11}H_3$]
	91.054415	C_7H_7+	2.070339	2535.49	[M – $C_{13}H_{13}$]



(f)

Parent ion	Secondary fragments				
C_32_H14+	**Center Mass (u)**	**Formula**	**Mass Deviation (ppm)**	**Area (intensity)**	**Neutral Loss**
(Ovalene)	394.077868	C_32H_10+	0.421509	215353.63	-
	392.062192	C_32H_8+	0.357463	201406.39	$[M - H_2]$
	152.061736	C_12H_8+	-2.075409	3864.36	$[M - C_{20}H_2]$
	139.054059	C_11H_7+	-1.205653	4964.57	$[M - C_{21}H_3]$
	128.062003	C_10H_8+	-0.377032	4006.6	$[M - C_{22}H_2]$

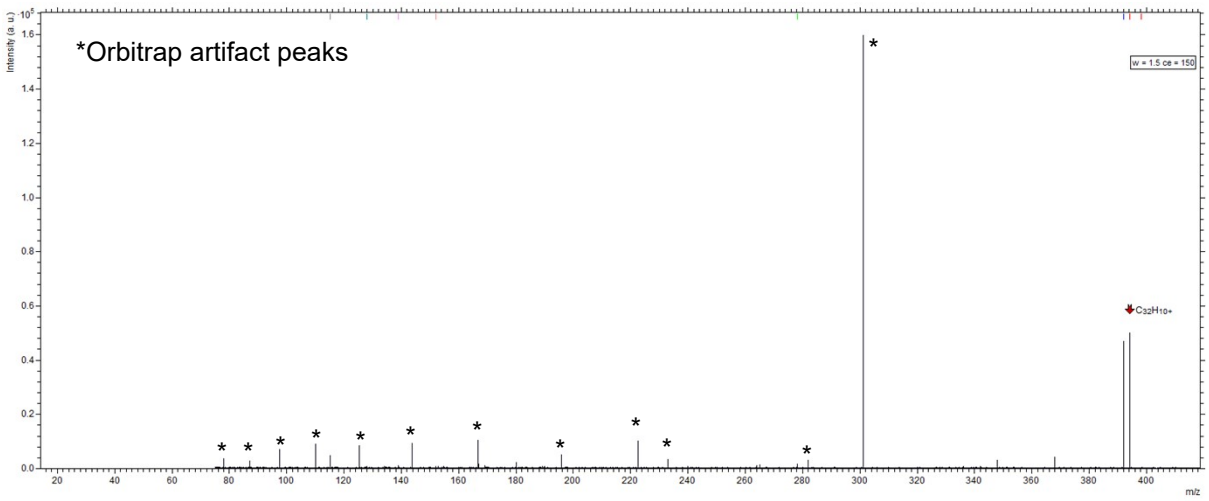
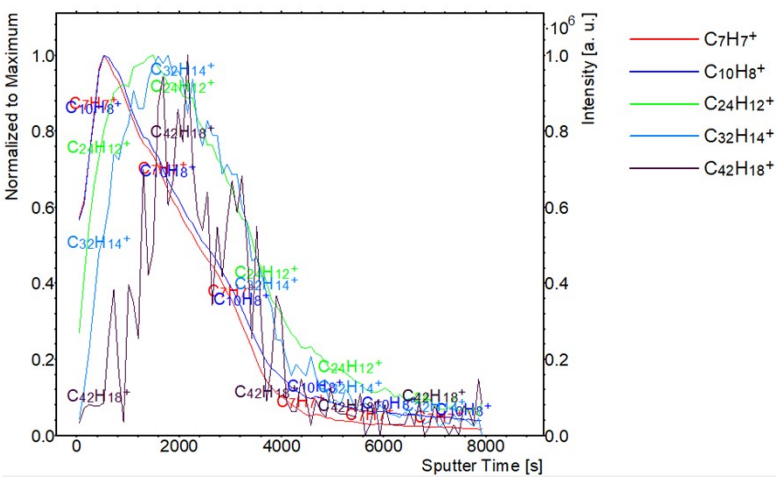


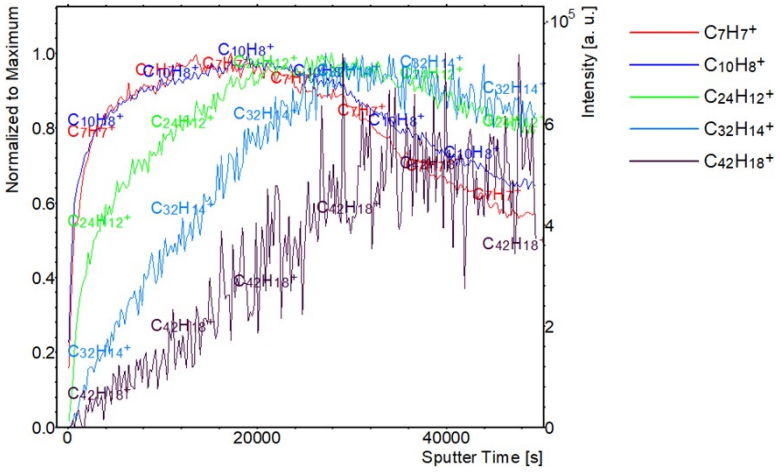
Fig. S7: MS/MS data for key PAHs with relevant spectra. **(a)** Anthracene ($C_{14}H_8^+$, NCE 100, IW 1.2 u), **(b)** $C_{14}H_{10}^+$ (NCE, 75 IW 1 u), **(c)** $C_{16}H_{10}^+$ (NCE 110, IW 1.2 u) **(d)** Coronene ($C_{24}H_{12}^+$, NCE 90, IW 0.4 u), **(e)** corannulene ($C_{20}H_{10}^+$, NCE 80, IW 5 u), **(f)** Ovalene ($C_{32}H_{14}^+$, NCE 150, IW 1.5). NCE, normalized collision energy. IW, isolation width. Where suitable, chemical structures and suggested fragments are assigned.

S8

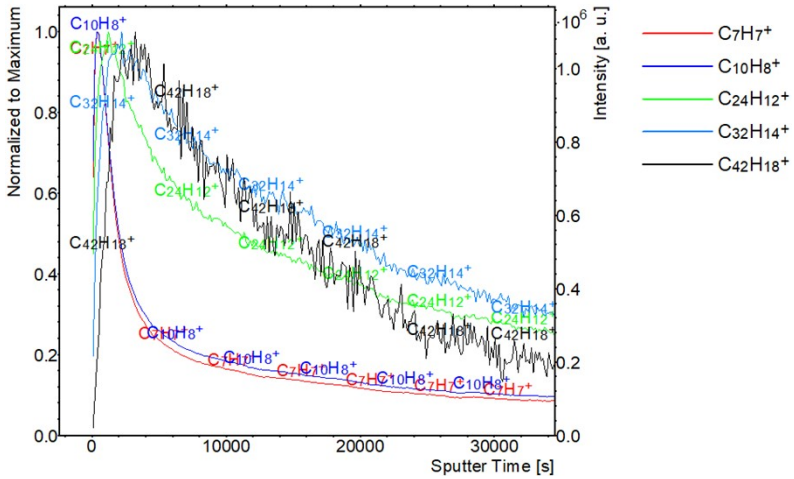
(a)



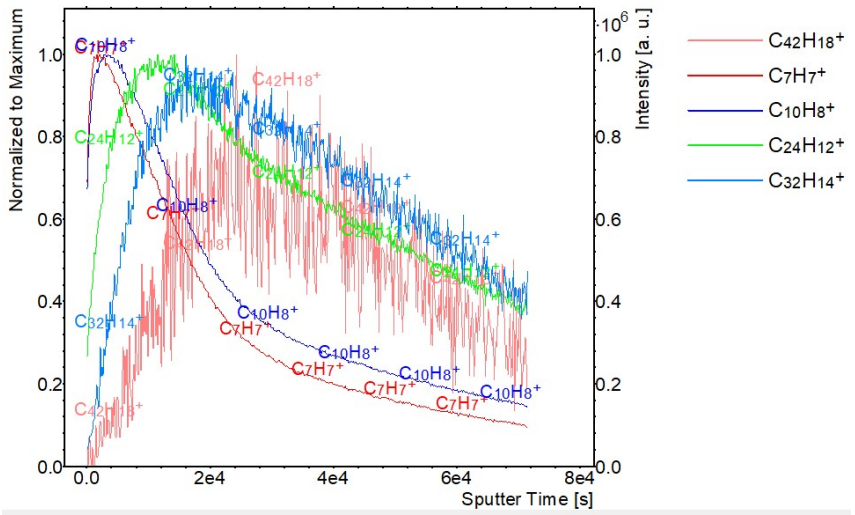
(b)


Normalized to Maximum
Intensity [a. u.]
Sputter Time [s]
C7H7+
C10H8+
C24H12+
C32H14+
C42H18+

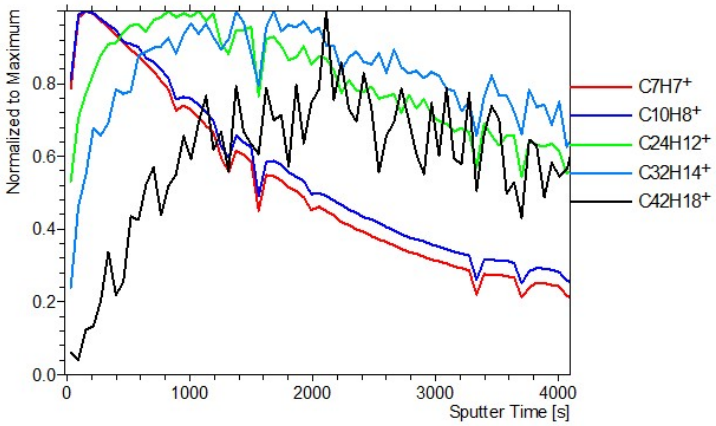
(c)


Normalized to Maximum
Intensity [a. u.]
Sputter Time [s]
C7H7+
C10H8+
C24H12+
C32H14+
C42H18+

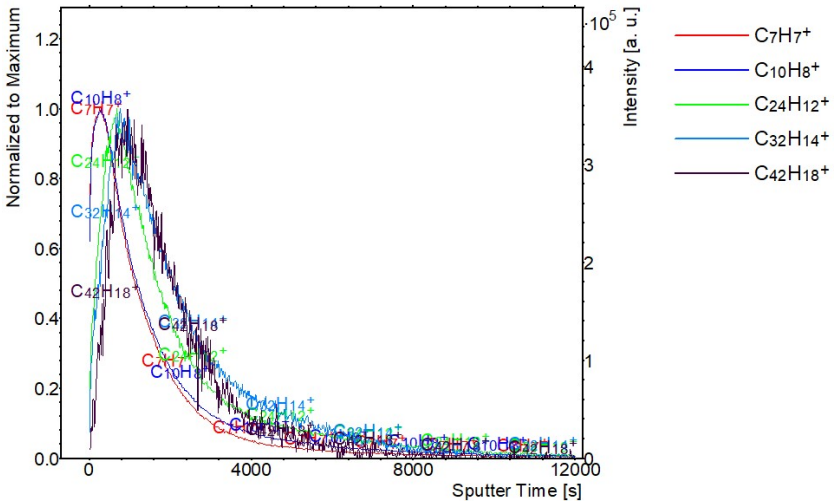
(d)


Normalized to Maximum
Intensity [a. u.]
Sputter Time [s]
C42H18+
C7H7+
C10H8+
C24H12+
C32H14+

(e)


Normalized to Maximum
Sputter Time [s]
C7H7+
C10H8+
C24H12+
C32H14+
C42H18+

(f)


Normalized to Maximum
Intensity [a. u.]
Sputter Time [s]
C7H7+
C10H8+
C24H12+
C32H14+
C42H18+

(g)

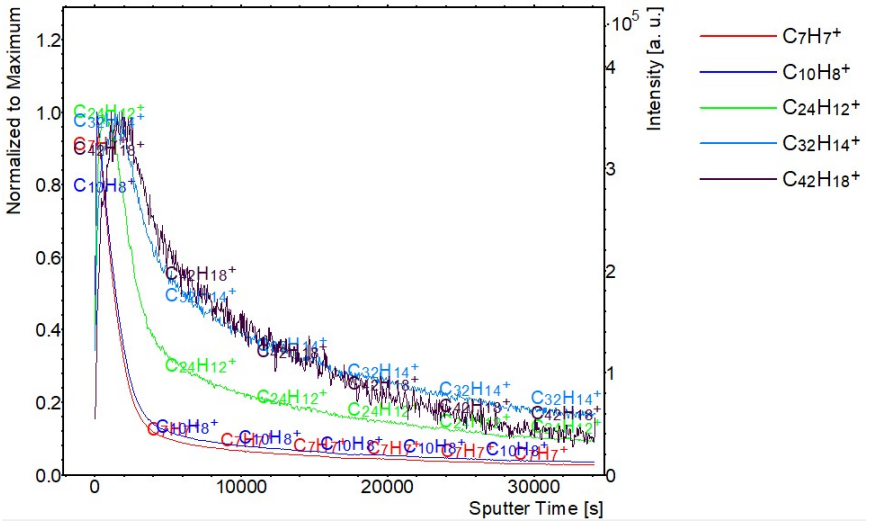


Fig. S8. Depth profile of polycyclic aromatic hydrocarbons in **(a)** Injector tip 1, **(b)** Injector tip 3, **(c)** Injector tip 4, **(d)** Injector tip 5, **(e)** Injector tip 6, **(f)** Injector tip 7, **(g)** Injector tip 8. Ions displayed are (in order of prevalence in the deposit $C_7H_7^+$, naphthalene ($C_{10}H_8^+$), coronene ($C_{24}H_{12}^+$), ovalene ($C_{32}H_{14}^+$) and hexabenzocoronene ($C_{42}H_{18}^+$).

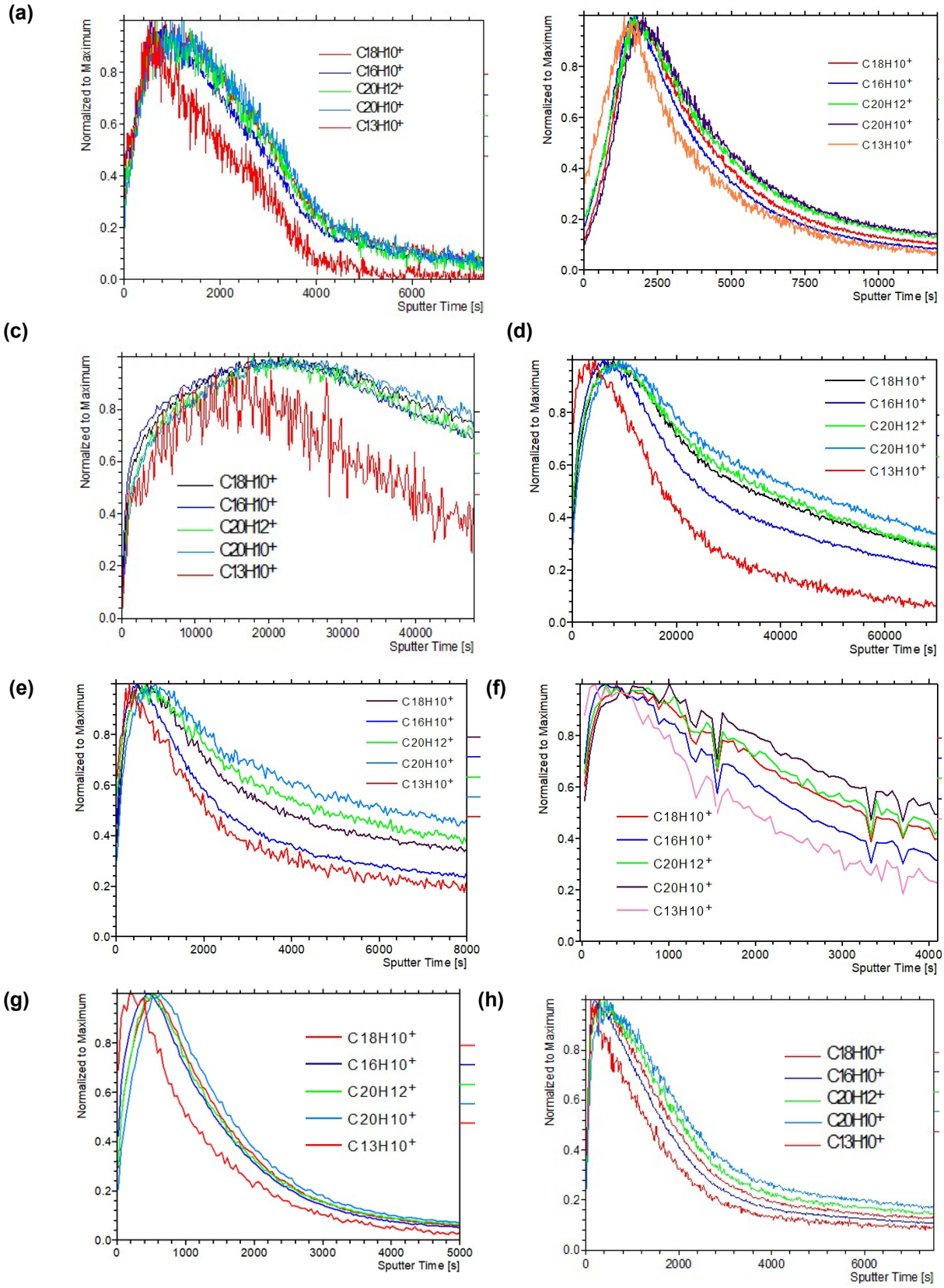
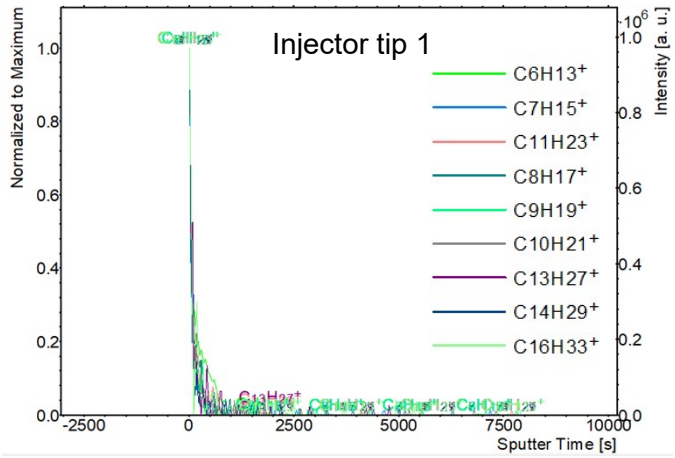
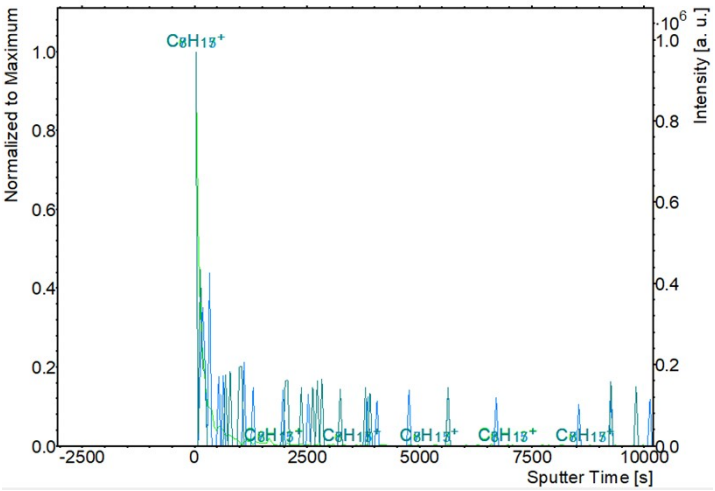


Fig. S9. Depth profiles of 5-membered PAHs in **(a)** Injector 1, **(b)** Injector 3, **(c)** Injector 4, **(d)** Injector 5, **(e)** Injector 6, **(f)** Injector 7, **(g)** Injector 8. Fluorene ($C_{13}H_{10}^{+}$,), cyclopentapyrene ($C_{18}H_{10}$) benzofluoranthene ($C_{20}H_{12}$) and corannulene ($C_{20}H_{10}$).

S10

(a)





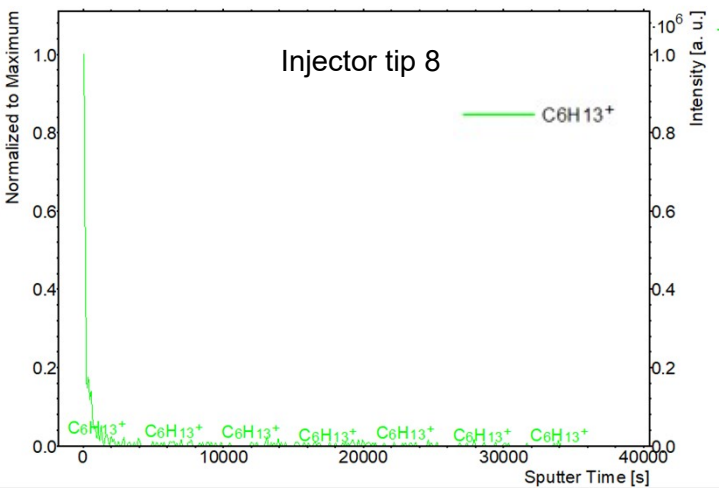


Fig. S10. Depth profiles of species with an aliphatic content for species which contained ions with enough intensity to provide an informative depth profile.

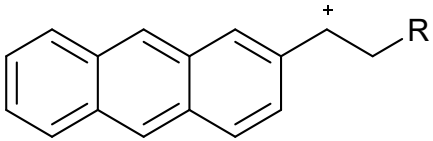
Table S11: 3D OrbiSIMS accurate mass data for hydrocarbons with an aliphatic contribution identified in injector tip deposits. (a) Saturated hydrocarbons, (b) species with an aromatic portion with putative assignments. All ion peak tables were exported from Surface Lab software (IONTOF GmbH, version 7.1.b).

(a)

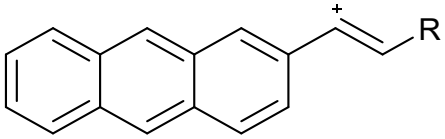
DBE = 0	Injector tip 1			Injector tip 2			Injector tip 5			Injector tip 8		
Assignment	Center Mass (u)	Deviation (ppm)	Area	Center Mass (u)	Deviation (ppm)	Area	Center Mass (u)	Deviation (ppm)	Area	Center Mass (u)	Deviation (ppm)	Area
C_6H_13+	85.101357	2.122838	749809.04	85.101397	2.591697	520115.87	85.101356	2.110708	360742.86	85.10136	2.155555	90294.38
C_7H_15+	99.116912	0.861387	50543.37	99.116951	1.248925	550369.03	99.116935	1.094524	16453.88			
C_8H_17+	113.132449	-0.246925	47467.83	113.132483	0.055611	542947.3	113.132475	-0.017477	17211.23			
C_9H_19+	127.148166	0.306492	54829.1	127.148144	0.132733	612927.87						
C_10H_21+	141.163834	0.40057	59568.13	141.163741	-0.257416	692567.65						
C_11H_23+	155.17948	0.340013	55623.57	155.17936	-0.432814	687630.37						
C_12H_25+	169.195153	0.449966	47177.68	169.19504	-0.221767	563652.12						
C_13H_27+	183.210912	1.005559	34290.37	183.210764	0.200537	519093.45						
C_14H_29+	197.226571	0.982382	32219.17	197.226424	0.234477	460484.38						
C_16H_33+	225.25761	-0.300503	20297.56	225.257687	0.040048	341267.53						
C_18H_37+	253.288776	-0.794989	9815.39	253.288941	-0.145126	220551.57						
C_21H_43+	295.33603	0.347652	6333.82	295.336029	0.342693	108209.86						
C_25H_51+	351.398296	-0.661624	4303.32	351.398593	0.185223	59168.75						

(b)

		Injector tip 1		
DBE = 10	Assignment	Center Mass (u)	Deviation (ppm)	Area
	C_17H_15+	219.116766	-0.27722	122739.98
	C_18H_17+	233.132374	-0.442115	10614.57
	C_39H_59+	527.461764	1.205452	5693.17
	C_41H_63+	555.492835	0.731157	7454.45
	C_46H_73+	625.570903	0.358158	11079.2
DBE = 11	Assignment	Center Mass (u)	Deviation (ppm)	Area
	C_17H_13+	217.101126	-0.233377	781418.24
	C_18H_15+	231.116775	-0.225365	113619.81
	C_19H_17+	245.132484	0.027457	37882.82
	C_20H_19+	259.148111	-0.063006	16549.84
	C_21H_21+	273.163774	-0.011466	31724.85
	C_22H_23+	287.179374	-0.184167	8732.67
	C_27H_33+	357.257685	0.021941	5289.19
	C_35H_49+	469.382855	-0.048915	4973.81



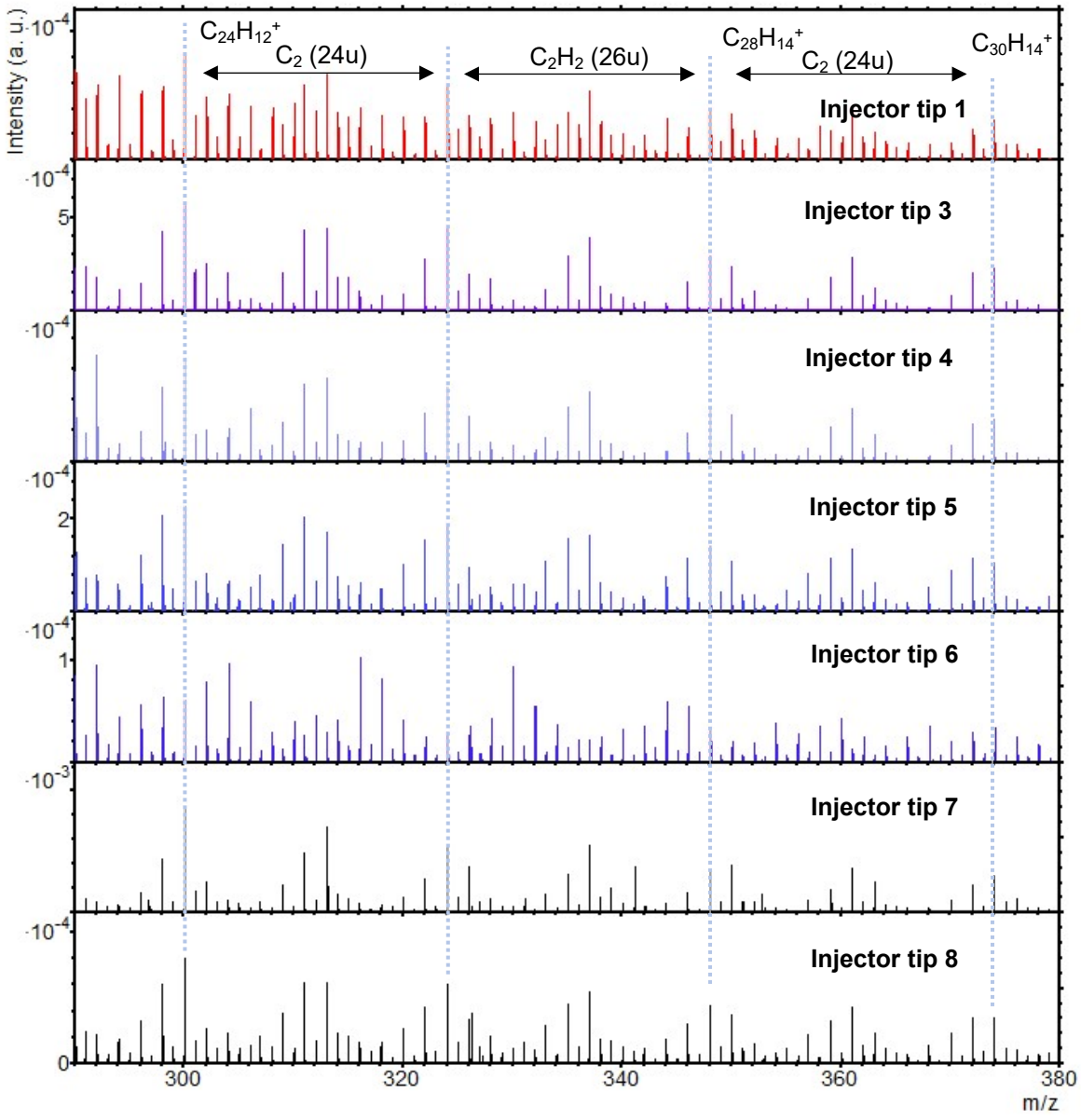
$R = C_nH_{(2n+1)}$



$R = C_nH_{(2n+1)}$

S12

(a)


Intensity (a. u.)
$C_{24}H_{12}^+$
C_2 (24u)
C_2H_2 (26u)
$C_{28}H_{14}^+$
C_2 (24u)
$C_{30}H_{14}^+$
Injector tip 1
Injector tip 3
Injector tip 4
Injector tip 5
Injector tip 6
Injector tip 7
Injector tip 8
300
320
340
360
380
m/z

(b)

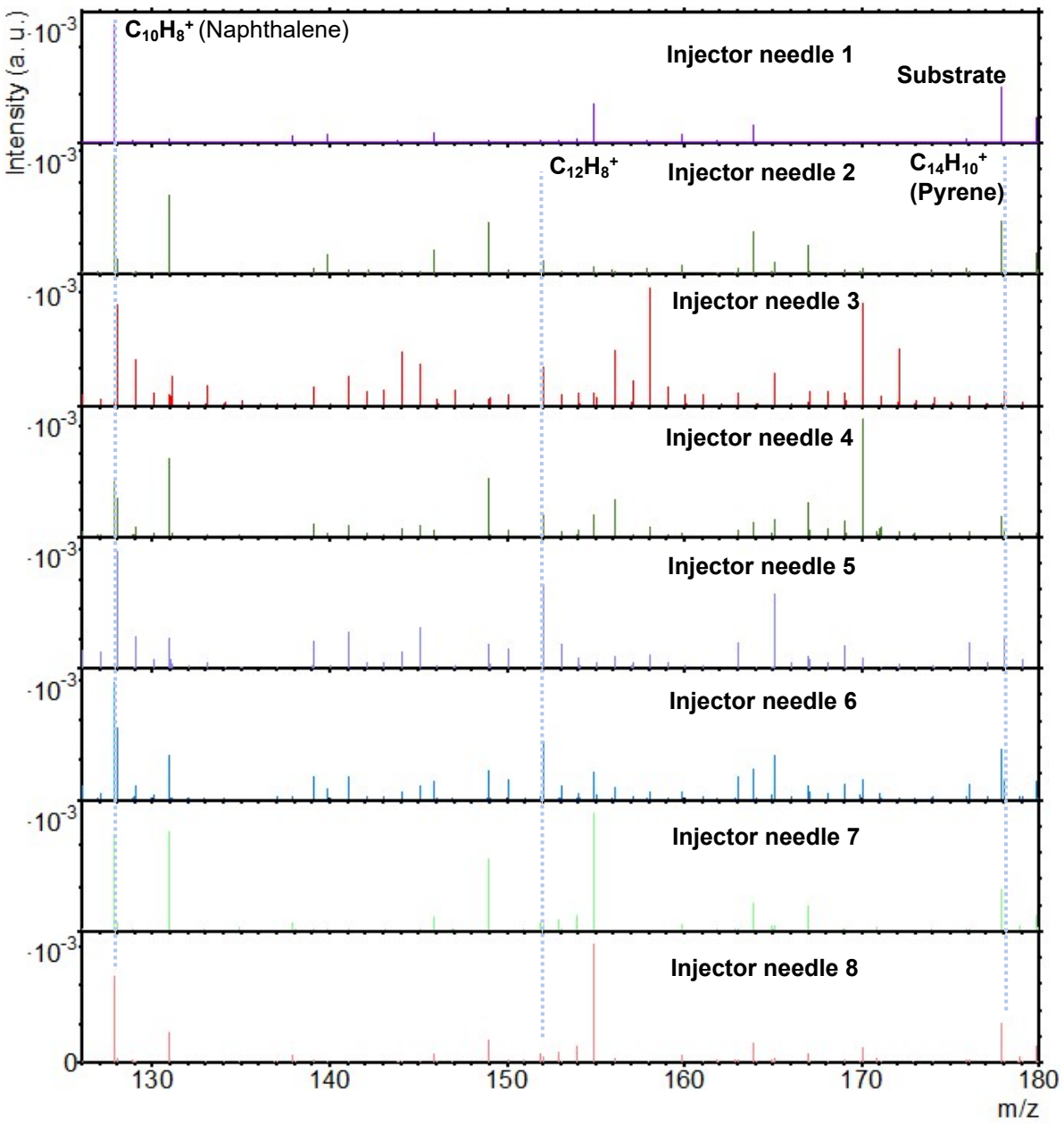


Fig. S12: Illustrating the peak separation corresponding to alternate C_2H_2 and C_2 addition from 3D OrbiSIMS spectral fragmentation. **(a)** injector tip deposits, **(b)** injector needle deposits. Injector needle 1 did not show strongly ionizing peaks for PAHs above naphthalene ($C_{10}H_8^+$) AU, arbitrary units.

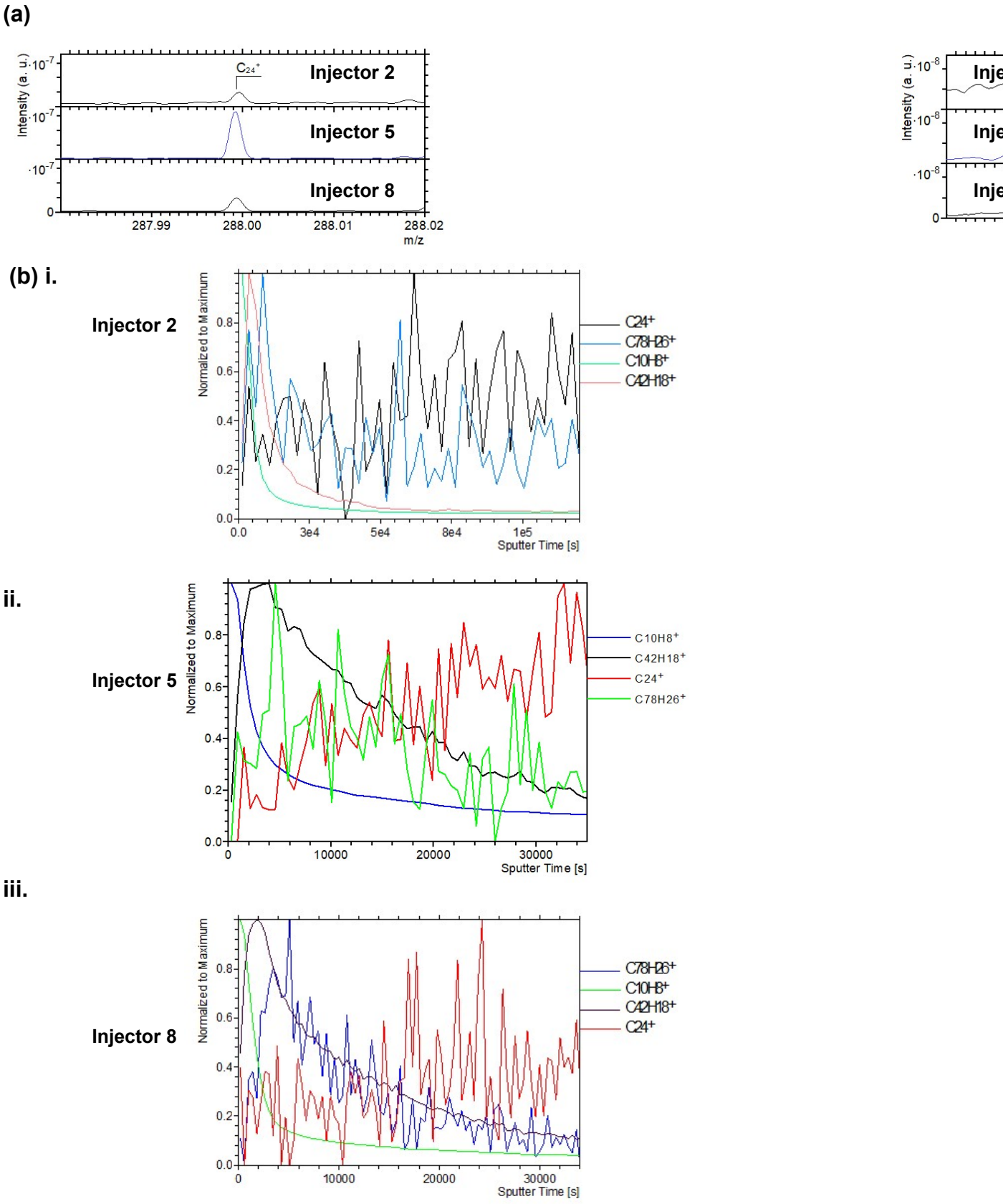
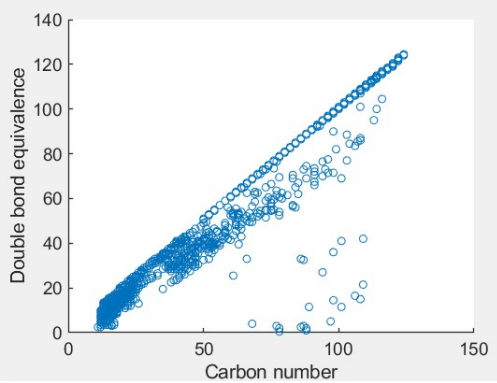
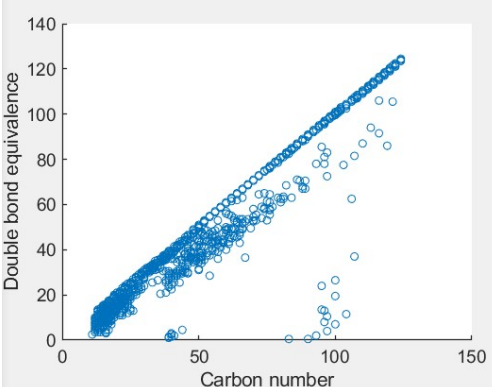


Fig. S13. Fullerenes in deposits. (a) 3D OrbiSIMS spectra showing molecular ion peaks for C_{24} and C_{28} peaks. **(b)** Depth profiles showing the behavior of the C_{24} fullerene compared to naphthalene, hexabenzocoronene and a large PAH, $C_{78}H_{26}^+$ in i. injector 2, iii. Injector 5 and ii. Injector tip 8.

(a)

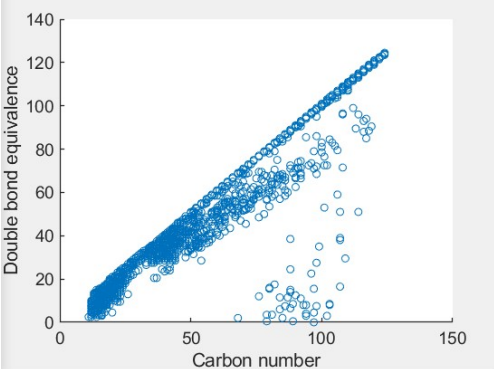


(b)

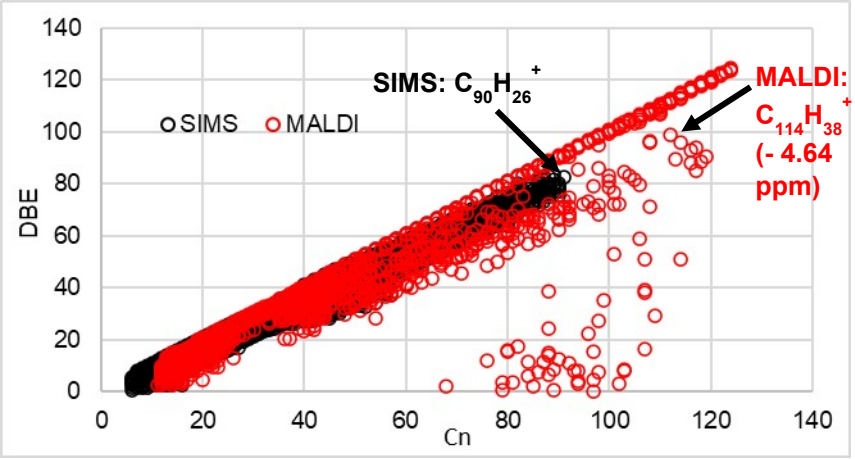


(c)

(d)



(e)



(f)

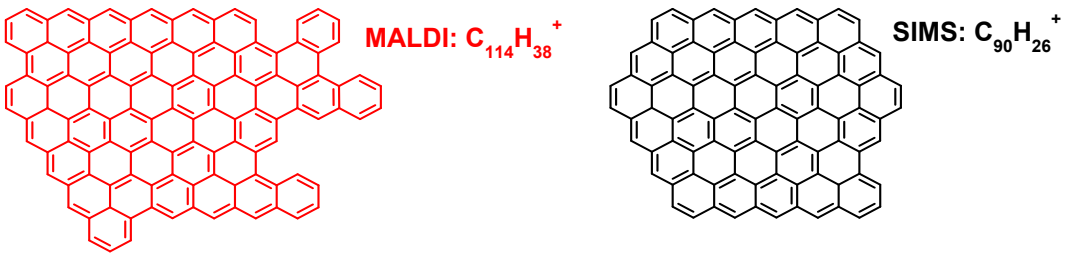


Fig. S14. (a – c) DBE v Cn of CH containing species (within a 6 ppm error range) from AP-MALDI analysis of injector tip deposit 5 using a TCNQ matrix for 3 analytical repeats. d) Spectral peak showing highest maximum mass PAH in MALDI data e) comparison of the SIMS and MALDI data with highest mass PAHs marked for each dataset. (f) putative chemical structure of largest ions.

S15

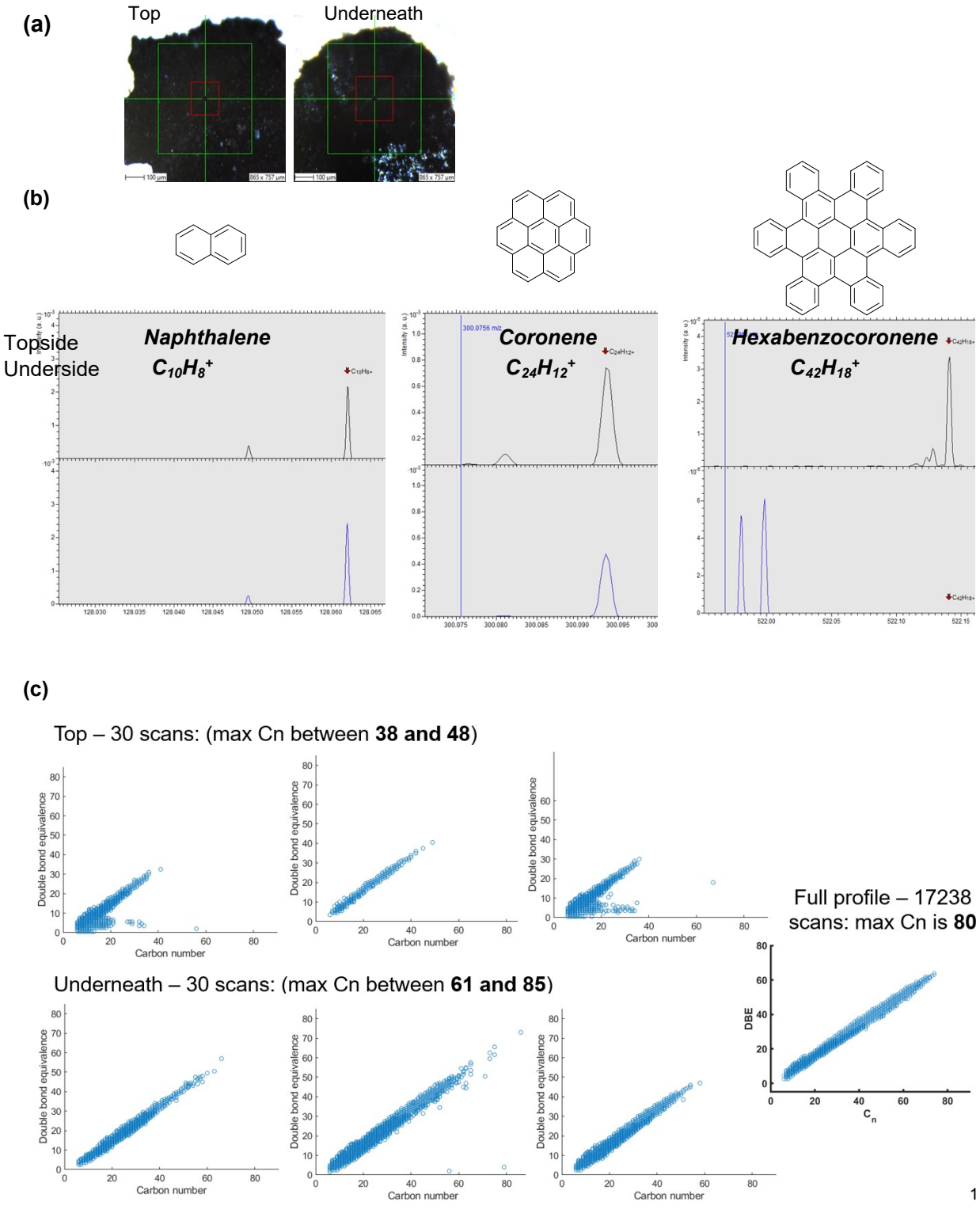
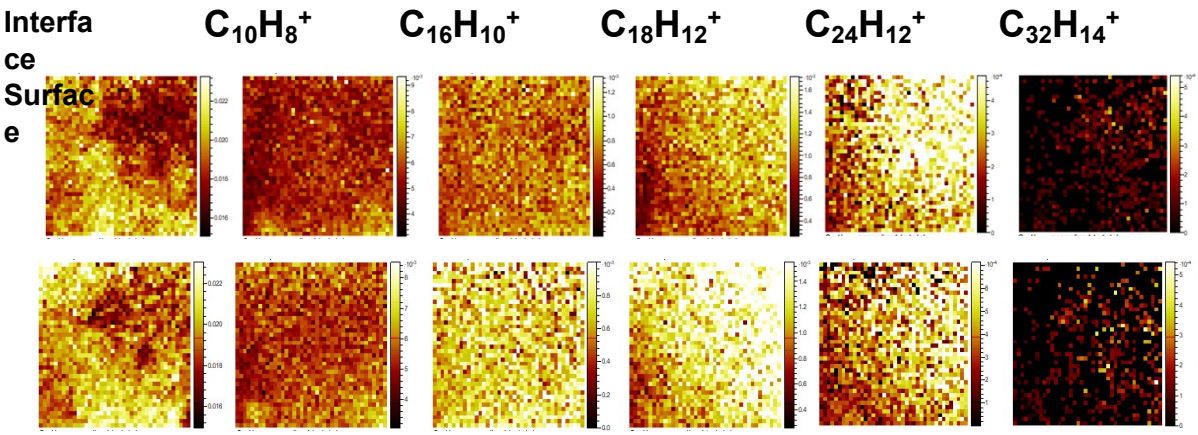


Fig. S15. a) Photograph of the deposit scraping used in the experiment, **b)** 3D OrbiSIMS spectra of 3 PAHs from the top and bottom side of a deposit scraping (30 scans), showing larger and more intense PAHs on the underside. **c)** Summary of all CH species under 2 ppm error from three analysis area with comparison to the depth profiling data.

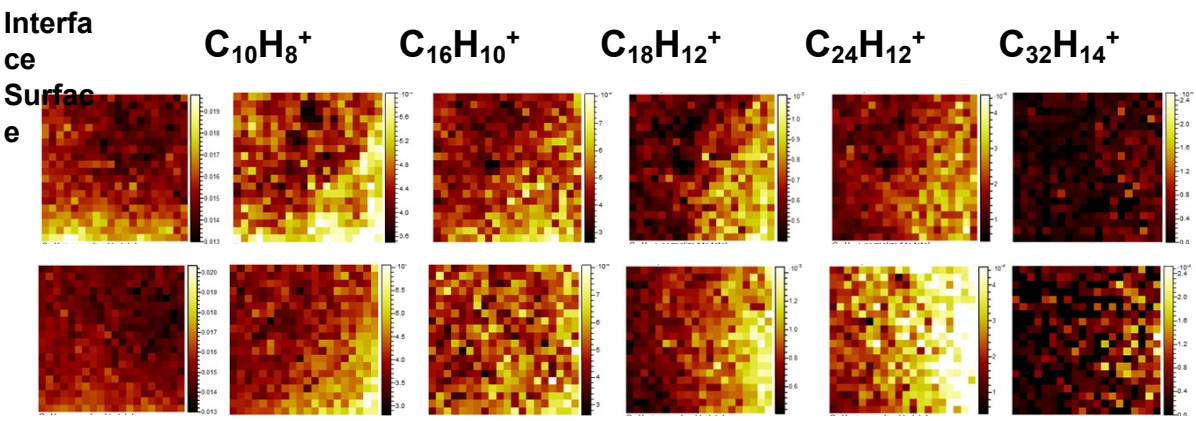
S16

(a) i.


Interface Surface
$C_{10}H_8^+$
$C_{16}H_{10}^+$
$C_{18}H_{12}^+$
$C_{24}H_{12}^+$
$C_{32}H_{14}^+$

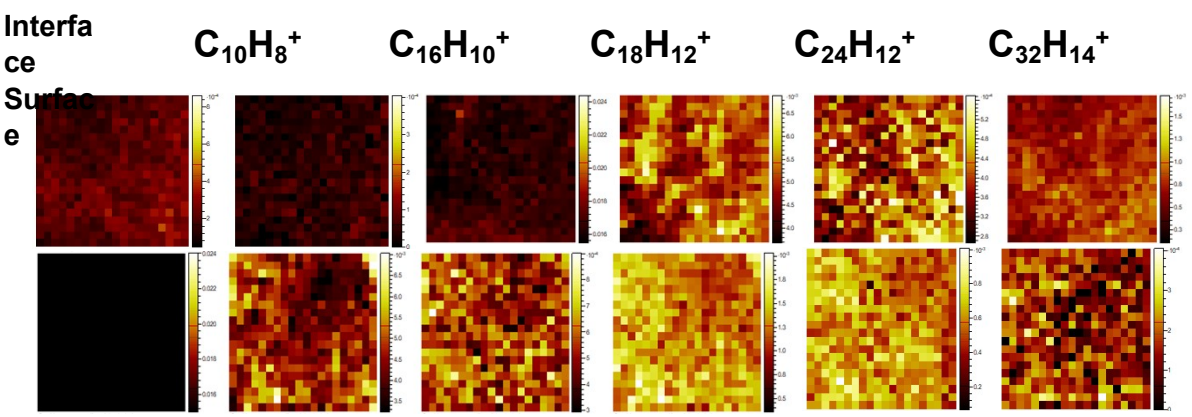
$C_{42}H_{18}^{+}$

ii.


Interface Surface
$C_{10}H_8^+$
$C_{16}H_{10}^+$
$C_{18}H_{12}^+$
$C_{24}H_{12}^+$
$C_{32}H_{14}^+$

$C_{42}H_{18}^{+}$

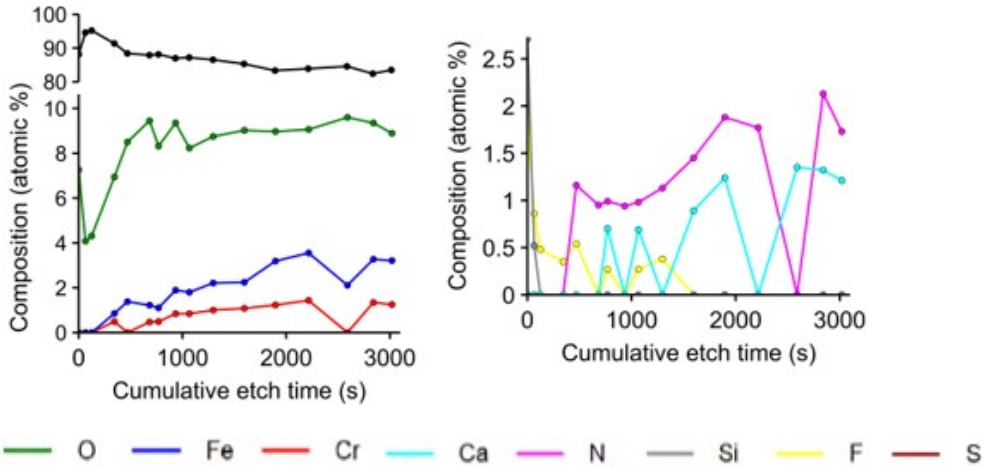
iii.


Interface Surface
$C_{10}H_8^+$
$C_{16}H_{10}^+$
$C_{18}H_{12}^+$
$C_{24}H_{12}^+$
$C_{32}H_{14}^+$

$C_{42}H_{18}^{+}$

Fig. S16. **(a)** Chemical images (200 x 200 μm, normalized to the total ion count) of key ions taken at the surface (above) and at a lower deposit depth after sputtering (below). **i**. Injector tip 1 (sputter time = 510 s. **ii**. Injector tip 2 (sputter time = 2650 s. **iii**. Injector tip 3 (sputter time = 1850 s).

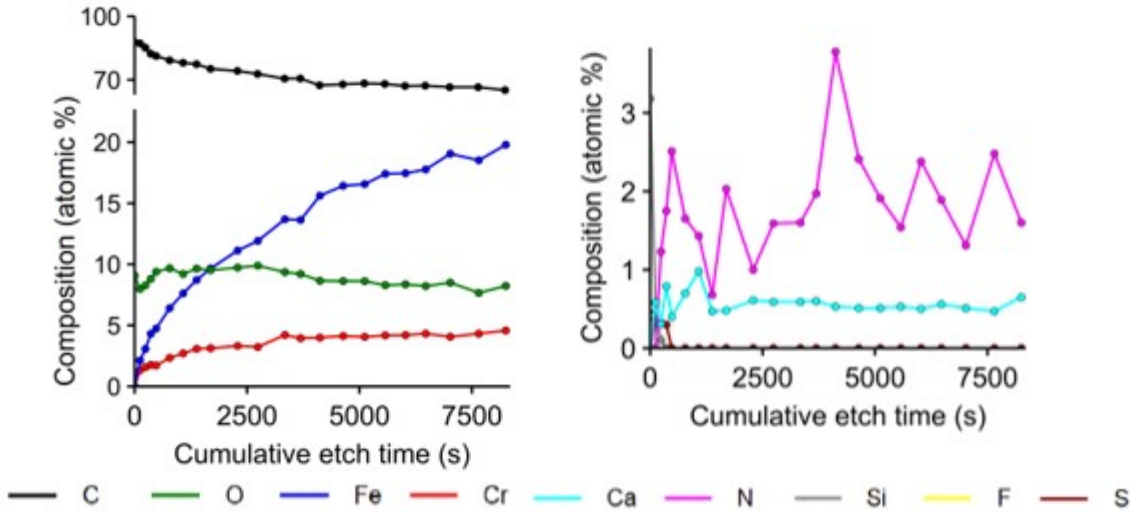
S17



	Element and atomic percentage							
Cumulative etch time (s)	C 1s	O 1s	Fe 2p	Cr 2p	Ca 2p	S 2p	Si 2s	N 1s
0	87.74	9.08	0	0	0	0	3.18	0
120	87.15	7.98	2.13	1.33	0.58	0.37	0.46	0
240	85.12	8.28	3.07	1.57	0.31	0.32	0.1	1.23
360	82.29	8.8	4.31	1.76	0.79	0.3	0	1.75
480	81.23	9.39	4.74	1.72	0.4	0	0	2.51
780	79.21	9.68	6.41	2.34	0.7	0	0	1.65
1080	78.04	9.21	7.62	2.71	0.98	0	0	1.43
1380	77.4	9.65	8.72	3.08	0.47	0	0	0.68
1691	75.18	9.52	9.66	3.13	0.48	0	0	2.03
2291	74.21	9.73	11.13	3.32	0.61	0	0	1
2741	72.77	9.89	11.92	3.23	0.59	0	0	1.59
3341	70.56	9.36	13.69	4.21	0.59	0	0	1.6
3691	70.63	9.21	13.63	3.95	0.6	0	0	1.97
4121	67.43	8.65	15.62	4	0.53	0	0	3.78
4638	67.88	8.63	16.43	4.13	0.51	0	0	2.41
5117	68.32	8.62	16.57	4.06	0.51	0	0	1.91
5574	68.06	8.29	17.41	4.18	0.53	0	0	1.54
6024	67.11	8.36	17.46	4.2	0.5	0	0	2.38
6474	67.25	8.22	17.77	4.32	0.56	0	0	1.89
7019	66.56	8.5	19.05	4.07	0.51	0	0	1.31
7653	66.54	7.66	18.52	4.32	0.47	0	0	2.48
8253	65.15	8.23	19.79	4.58	0.65	0	0	1.6

(a)

(b)



Etch Time (s)	C158	O158	Fe158	Cr158	Ca158	S158	Si158	N158
0	87.74	9.08	0	0	0	0	3.18	0
120	87.15	7.98	2.13	1.33	0.58	0.37	0.46	0
240	85.12	8.28	3.07	1.57	0.31	0.32	0.1	1.23
360	82.29	8.8	4.31	1.76	0.79	0.3	0	1.75
480	81.23	9.39	4.74	1.72	0.4	0	0	2.51
780	79.21	9.68	6.41	2.34	0.7	0	0	1.65
1080	78.04	9.21	7.62	2.71	0.98	0	0	1.43
1380	77.4	9.65	8.72	3.08	0.47	0	0	0.68
1691	75.18	9.52	9.66	3.13	0.48	0	0	2.03
2291	74.21	9.73	11.13	3.32	0.61	0	0	1
2741	72.77	9.89	11.92	3.23	0.59	0	0	1.59
3341	70.56	9.36	13.69	4.21	0.59	0	0	1.6
3691	70.63	9.21	13.63	3.95	0.6	0	0	1.97
4121	67.43	8.65	15.62	4	0.53	0	0	3.78
4638	67.88	8.63	16.43	4.13	0.51	0	0	2.41
5117	68.32	8.62	16.57	4.06	0.51	0	0	1.91
5574	68.06	8.29	17.41	4.18	0.53	0	0	1.54
6024	67.11	8.36	17.46	4.2	0.5	0	0	2.38
6474	67.25	8.22	17.77	4.32	0.56	0	0	1.89
7019	66.56	8.5	19.05	4.07	0.51	0	0	1.31
7653	66.54	7.66	18.52	4.32	0.47	0	0	2.48
8253	65.15	8.23	19.79	4.58	0.65	0	0	1.6

Fig. S17. X-ray photoelectron spectroscopy elemental depth profile results using an Ar_{500}^{+} etching beam on (a), injector tip 1 and (b) injector tip 2.

Table S18: 3D OrbiSIMS ion table for nitrogen containing ions identified in **(a)** injector tip deposits **i.** injector tips 1-4, **ii.** Injector tips 5-8. **(b)** injector needle deposits All ion peak tables were exported from Surface Lab software (IONTOF GmbH, version 7.1.b). Deviation (ppm) refers to the difference between the observed and expected ion mass. The observed mass is measured as the center mass of the ion peak.

(a) i.

Assignment	Injector tip 1			Injector tip 2			Injector tip 3			Injector tip 4		
Alkyl phenyl pyridine	Center Mass (u)	Deviation (ppm)	Area (Intensity)	Center Mass (u)	Deviation (ppm)	Area (Intensity)	Center Mass (u)	Deviation (ppm)	Area (Intensity)	Center Mass (u)	Deviation (ppm)	Area (Intensity)
C_12H_12N+	170.096511	0.498507	756476972.7	170.096382	-0.258774	2125402742	170.096231	-1.145983	719054730.9	170.096287	-0.816251	1703323931
C_13H_14N+	184.112229	0.829357	814005776.7	184.112104	0.154806	2004051970	184.111944	-0.715156	540500820	184.112007	-0.375943	2079875430
C_14H_16N+	198.127901	0.883809	532747793.8	198.127761	0.175291	932152860.2	198.12757	-0.784895	226801461.1	198.127628	-0.492281	1355005064
C_15H_18N+	212.14347	0.444577	239141572.7	212.14339	0.06393	304235090.5	212.143302	-0.350963	80326160.15	212.143338	-0.180226	562003332.3
C_16H_20N+	226.158977	-0.215925	90219871.04	226.158957	-0.30681	82484622.68	226.159024	-0.008516	23300378.78	226.159023	-0.014091	201954905.4
C_17H_22N+	240.17456	-0.483257	31045829.73	240.174571	-0.435648	23701271.64	240.174652	-0.100298	3443264.85	240.174665	-0.045176	58708024.22
Benzoquinoline												
C_9H_8N+	130.065191	0.501077	63579739.9	130.065132	0.05107	664401674.5	130.06504	-0.657868	113566957.6	130.065061	-0.494778	544263419.7
C_13H_10N+	180.080857	0.449847	96394302.94	180.080738	-0.208299	601226701.6	180.080574	-1.121618	241266795.8	180.080604	-0.952272	499572336.9
C_17H_12N+	230.096355	-0.308254	25731135.36	230.096434	0.035462	222112398.8	230.096457	0.134972	101548612.3	230.096444	0.076994	246884527.9
C_19H_12N+	254.096303	-0.484997	15979704.92	254.096365	-0.23934	167878516.9	254.096399	-0.10578	71136173.9	254.096371	-0.216779	114010522
C_23H_14N+	304.112045	-0.102498	4699548.36	304.112087	0.035305	49819119.05	304.11211	0.110598	19276497.48	304.112092	0.054196	28027983.43
C_25H_14N+	328.11215	0.224781	3308215.41	328.112189	0.345858	38889492.01	328.112193	0.356933	14593165.19	328.112179	0.313746	21198225.23
C_29H_16N+	378.12765	-0.201461	983772.9	378.127732	0.01659	12479313.49	378.127728	0.004962	2763353.05	378.127761	0.093615	4179549.4
C_31H_16N+	402.127644	-0.204412	735389.64	402.127748	0.05369	10523177.37	402.127722	-0.008569	2292424.21	402.127782	0.139673	3387187.88
C_35H_17N+	451.135537	-0.031428	114334.85	451.135651	0.220662	2383173.12	451.135587	0.07943	430924.27	451.135619	0.151457	722160.72
Alkyl quinoline												
C_10H_10N+	144.080845	0.481256	74220691.05	144.080751	-0.173888	629673627.5	144.080622	-1.069946	94479734.82	144.080656	-0.834386	771474216.1
C_11H_12N+	158.09648	0.343249	67050260.94	158.096373	-0.333695	301542081.4	158.096248	-1.12457	44234088.8	158.096284	-0.895181	665021237.9
C_12H_14N+	172.112067	-0.048795	33894545.68	172.111939	-0.793897	63849737.24	172.111847	-1.328902	6444577.96	172.111871	-1.18803	136015885.9
C_13H_16N+	186.127777	0.271985	9947215.89	186.127654	-0.383899	15408256.24	186.127573	-0.821654	815299.39	186.127611	-0.619876	20262679.09
Carbazole												
C_12H_10N+	168.08085	0.439041	164761068.1	168.080722	-0.322048	694638476.1	168.08057	-1.222109	330411933.1	168.080612	-0.972163	705144355.1
C_14H_12N+	194.096589	0.838526	82157736.21	194.096458	0.166582	418787465.8	194.096297	-0.664023	163130400.3	194.09632	-0.545144	346557909.7

C_20H_14N+	268.111957	-0.4418	10148034.48	268.112015	-0.227507	87892658.56	268.112073	-0.010727	37575276.97	268.112058	-0.067398	58152188.03
C_24H_16N+	318.127684	-0.133335	2611704.27	318.12773	0.011889	24565328.05	318.127755	0.092343	7424808.81	318.127752	0.08074	10850133.33
C_30H_20N+	394.158904	-0.308823	59041.85	394.159053	0.067567	984047.42	394.159052	0.065579	137200.22	394.159052	0.065961	199957.04

ii.

Assignment	Tip 5 (159)			Tip 6 (161)			Tip 7 (GM15)			Tip 8 (GM20)		
Alkyl phenyl pyridine	Center Mass (u)	Deviation (ppm)	Area (Intensity)	Center Mass (u)	Deviation (ppm)	Area (Intensity)	Center Mass (u)	Deviation (ppm)	Area (Intensity)	Center Mass (u)	Deviation (ppm)	Area (Intensity)
C_12H_12N+	170.09616	-1.564358	5196728487	170.095952	-2.788304	1997684036	170.096124	-1.777287	15551033.2	170.096167	-1.523339	2686935792
C_13H_14N+	184.111853	-1.208977	6536969746	184.111662	-2.247666	1343833612	184.111841	-1.27743	12778919.83	184.111871	-1.110751	3628249301
C_14H_16N+	198.127486	-1.209335	4325605324	198.12737	-1.797998	534613983	198.127467	-1.304837	5100404.21	198.127509	-1.095334	2376915008
C_15H_18N+	212.143208	-0.790566	1798055467	212.143141	-1.106284	188069403.7	212.14319	-0.876476	1695818.36	212.143229	-0.69414	993273682.9
C_16H_20N+	226.158868	-0.700654	607978348.8	226.15882	-0.91107	57339528.73	226.15889	-0.601894	491140.08	226.158866	-0.709262	331394654.2
C_17H_22N+	240.174422	-0.435648	201870765.2	240.174205	-1.959843	14348227.07	240.174516	-0.667462	107407.88	240.17439	-1.192499	97889945.55
Benzoquinoline												
C_9H_8N+	130.064971	-1.192605	578111287.5	130.064923	-1.557158	76553697.39	130.065015	-0.851358	101474357.2	130.064992	-1.028595	719985079.5
C_13H_10N+	180.080476	-1.665979	596574925.4	180.080463	-1.738122	72791635.18	180.080481	-1.634177	24754800.1	180.08053	-1.363394	828958570.9
C_17H_12N+	230.09623	-0.850152	232141948.6	230.09616	-1.155707	24949629.8	230.096285	-0.613252	21086795.76	230.09633	-0.417798	522811246.6
C_19H_12N+	254.096144	-1.108221	117455425.5	254.096044	-1.50426	7381411.5	254.096199	-0.893655	16631508.88	254.096178	-0.976083	240149664.3
C_23H_14N+	304.111918	-0.51987	29821635.63	304.111847	-0.753517	1631872.18	304.111943	-0.436945	5976649.53	304.111948	-0.419394	70318831.68
C_25H_14N+	328.112037	-0.117807	22789687.52	328.112045	-0.092728	932598.03	328.112053	-0.070644	5389444.3	328.112071	-0.01499	55107451.7
C_29H_16N+	378.127454	-0.720391	6336566.5	378.131476	9.917129	575902.1	378.127498	-0.601575	2734911.43	378.127515	-0.556636	23646556.13
C_31H_16N+	402.127431	-0.733701	5571040.21	402.131568	9.553538	389520.85	402.127482	-0.607737	2425068.55	402.127527	-0.495212	20243716.79
C_35H_17N+	451.135266	-0.630722	1342611.08	451.136048	1.102508	70362.35	451.13536	-0.42303	675568.72	451.135432	-0.262651	6024489.05
Alkyl quinoline												
C_10H_10N+	144.080545	-1.598046	930572876.3	144.080492	-1.96774	117787488.1	144.080592	-1.278696	104568185.3	144.080567	-1.448637	831074189.1
C_11H_12N+	158.096152	-1.731075	870101419.4	158.096038	-2.449847	89516993.62	158.096195	-1.458305	53789318.05	158.096165	-1.646969	505274847.6
C_12H_14N+	172.111703	-2.164953	247727955.6	172.111451	-3.630718	25371235.61	172.111759	-1.84022	10243595.09	172.111717	-2.086172	136486135.3
C_13H_16N+	186.127379	-1.865947	75274061.65	186.127059	-3.584664	5281477.73	186.127485	-1.29419	1844775.1	186.127394	-1.784002	32513020.3

Carbazole												
C_12H_10N+	168.080506	-1.606504	1350448460	168.080538	-1.412227	168868270	168.080483	-1.744282	15052246.2	168.080522	-1.510469	1217322210
C_14H_12N+	194.096166	-1.336027	435557046.6	194.096124	-1.55631	63067031.03	194.096186	-1.235079	13416109.56	194.096213	-1.094577	564754392.6
C_20H_14N+	268.111813	-0.981989	69209864.37	268.111593	-1.800201	5796362.98	268.111854	-0.828726	8080842.08	268.111818	-0.962554	154504142.9
C_24H_16N+	318.127503	-0.701422	16697097.68	318.127477	-0.781219	1523911.8	318.127537	-0.594723	3666300.33	318.127522	-0.642455	55601751
C_30H_20N+	394.158796	-0.584273	344220.01	394.159103	0.195481	51896.1	394.158825	-0.508856	286937.82	394.158843	-0.465621	3371079.25

(b) i.

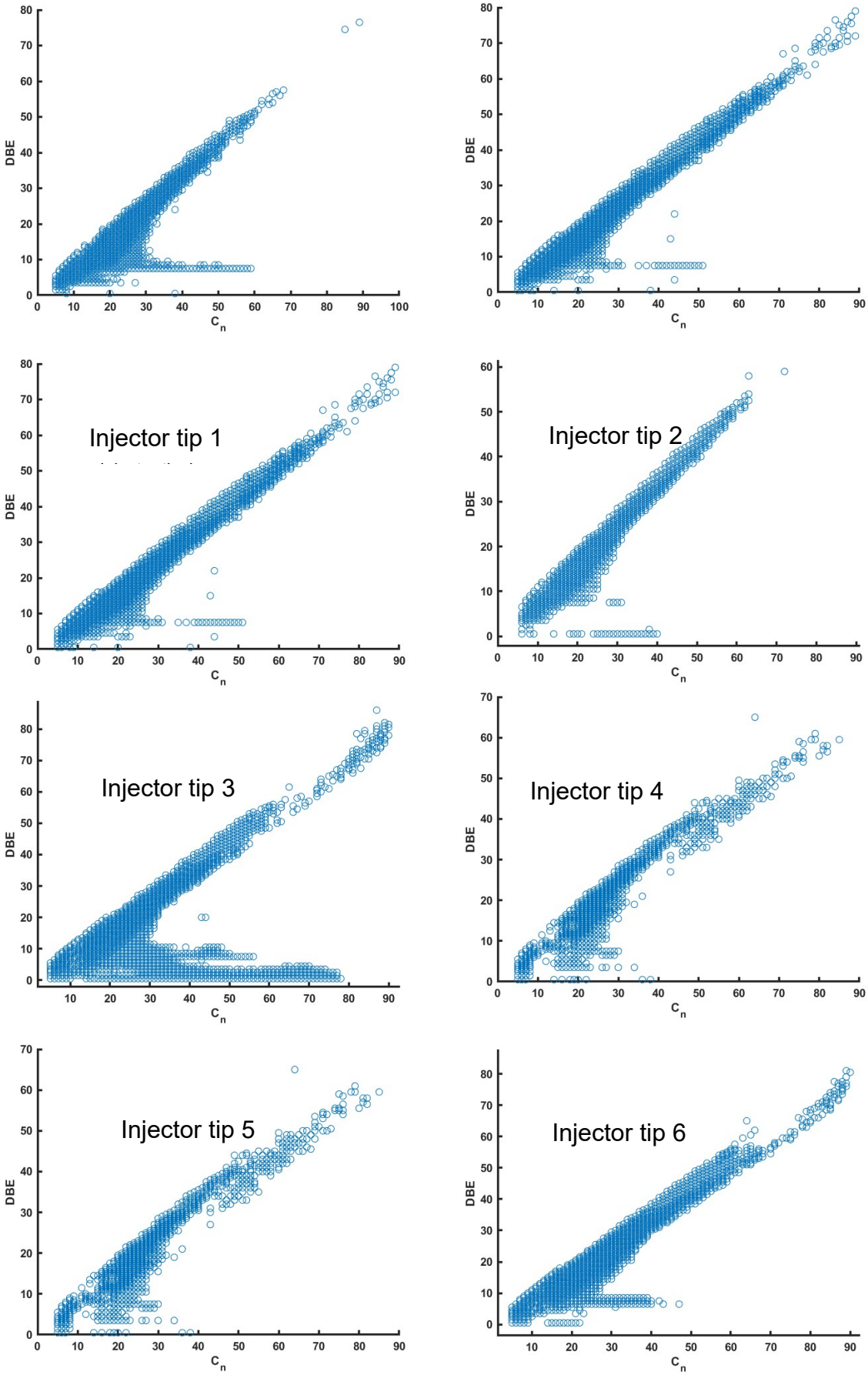
Assignment	**Injector needle 1**			**Injector needle 2**			**Injector needle 3**			**Injector needle 4**		
Alkyl phenyl pyridine	Center Mass (u)	Deviation (ppm)	Area (Intensity)	Center Mass (u)	Deviation (ppm)	Area (Intensity)	Center Mass (u)	Deviation (ppm)	Area (Intensity)	Center Mass (u)	Deviation (ppm)	Area (Intensity)
C_12H_12N+	170.096203	-1.312168	2948608.28	170.096264	-0.954112	842358.27	170.096273	-0.901188	1093711.72	170.096263	-0.960003	9662485.84
C_13H_14N+	184.111938	-0.746771	7328028.69	184.111983	-0.501936	928981.41	184.111988	-0.478289	738338.2	184.111977	-0.537333	12928395.91
C_14H_16N+	198.127575	-0.76429	10153921.67	198.127605	-0.612498	498249.48	198.127621	-0.528443	438760.39	198.127598	-0.647315	8558795.69
C_15H_18N+	212.14334	-0.171508	7468490.47	212.143313	-0.29876	214805.13	212.143339	-0.172144	280816.5	212.143316	-0.284406	3894237.1
C_16H_20N+	226.159043	0.07659	3655397.11	226.159034	0.036622	87687.4	226.159055	0.126242	159390.38	226.158975	-0.227677	1580106.69
C_17H_22N+	240.174631	-0.188004	1392886.51	240.174736	0.251242	35653.09	240.174724	0.197538	62802.51	240.174599	-0.32078	529379.59
Benzoquinoline												
C_9H_8N+	130.065025	-0.774668	780859.15	130.065089	-0.279206	304770.09	130.065094	-0.243416	921117.68	130.065042	-0.643493	295635.81
C_13H_10N+	180.080522	-1.410001	413485.72	180.080592	-1.020355	251363.03	180.080625	-0.839667	680123.34	180.080567	-1.160369	271577.49
C_17H_12N+	230.096439	0.057105	1134653.08	230.096452	0.112926	88259.64	230.096491	0.28273	787533.7	230.096425	-0.005394	147247.6
C_19H_12N+	254.096378	-0.189888	85629.26	254.09634	-0.33927	35710.75	254.096437	0.042286	247203.22	254.096358	-0.265672	25921
C_23H_14N+	304.112096	0.06656	13707.36	x	x	x	304.112198	0.403081	61269.32	x	x	x
C_25H_14N+	x	x	x	x	x	x	328.112286	0.639643	36688.59	x	x	x
C_29H_16N+	x	x	x	x	x	x	x	x	x	x	x	x
C_31H_16N+	x	x	x	x	x	x	x	x	x	x	x	x
C_35H_17N+	x	x	x	x	x	x	x	x	x	x	x	x
Alkyl quinoline												

C_10H_10N+	144.080603	-1.197044	2716921.17	144.080667	-0.757102	369446.64	144.08068	-0.665259	1658561.16	144.080614	-1.122555	684873.66
C_11H_12N+	158.096233	-1.218944	3836676.23	158.096283	-0.90094	329102.03	158.096305	-0.765956	1449851.98	158.09623	-1.236105	964716.39
C_12H_14N+	172.111823	-1.468447	1794651.86	172.111867	-1.216315	107405.67	172.111898	-1.032169	445584.06	172.111821	-1.479955	500788.15
C_13H_16N+	186.127518	-1.117973	688712.54	186.127604	-0.655251	25210.58	186.127645	-0.436997	106358.25	186.127553	-0.930401	175463.72
Carbazole												
C_12H_10N+	168.080524	-1.495448	737507.54	168.080597	-1.061539	295215.68	168.080614	-0.964362	594314.5	168.080555	-1.310804	775103.13
C_14H_12N+	194.096244	-0.934857	493487.65	194.096326	-0.515498	178631.61	194.096351	-0.384326	463066.84	194.096281	-0.744935	256064.96
C_20H_14N+	268.112089	0.048789	52977.68	268.112172	0.360252	13653.45	268.112105	0.109683	114489.02	268.112069	-0.026765	15450.46
C_24H_16N+	318.127715	-0.033759	22791.9	x	x	x	318.127815	0.278978	37409.2	318.127696	-0.095068	2389.93
C_30H_20N+	x	x	x	x	x	x	x	x	x	x	x	x

ii.

Assignment	Injector needle 5 (159)			Injector needle 6			Injector needle 7			Injector needle 8		
Alkyl phenyl pyridine	Center Mass (u)	Deviation (ppm)	Area (Intensity)	Center Mass (u)	Deviation (ppm)	Area (Intensity)	Center Mass (u)	Deviation (ppm)	Area (Intensity)	Center Mass (u)	Deviation (ppm)	Area (Intensity)
C_12H_12N+	170.096231	-1.144112	46360082.66	170.096202	-1.313197	1002722.86	170.096122	-1.788805	84291.58	170.096154	-1.596327	2808740.93
C_13H_14N+	184.111944	-0.71704	52522160.56	184.111911	-0.897591	768282.25	184.111799	-1.501502	78896.94	184.111857	-1.186918	4037296.75
C_14H_16N+	198.127558	-0.845727	33947407.65	198.127522	-1.02771	374424.93	198.127488	-1.199882	34000.76	198.127476	-1.261188	2550818.76
C_15H_18N+	212.143274	-0.480765	16118587.02	212.143246	-0.613591	172429.67	212.143187	-0.890564	13767.23	212.143217	-0.749733	1010975.53
C_16H_20N+	226.158971	-0.243906	7692459.45	226.158958	-0.302126	83044.77	x	x	x	226.158795	-1.02285	306271.26
C_17H_22N+	240.17459	-0.360116	3439496.48	240.174626	-0.207814	27711.3	x	x	x	240.174456	-0.914784	80135.17
Benzouinoline												
C_9H_8N+	130.065043	-0.636211	6021337.9	130.065042	-0.642892	210097.66	130.065073	-0.402268	338984.73	130.064972	-1.185344	99871.06
C_13H_10N+	180.080536	-1.33077	3434370.74	180.080564	-1.17331	159714.3	180.0805	-1.531354	50389.09	180.080468	-1.709039	88846.08
C_17H_12N+	230.09641	-0.069355	2071942.43	230.096391	-0.151706	100855.1	230.096282	-0.625474	26217.5	230.096285	-0.613441	46916.71
C_19H_12N+	254.096339	-0.341327	818415.47	254.096318	-0.426014	31382.03	254.096182	-0.960188	17013.45	254.096233	-0.758836	19858.48
C_23H_14N+	304.112066	-0.033321	106124.58	x	x	x	304.111878	-0.649711	2546.59	304.111997	-0.260606	5925.76
C_25H_14N+	328.112165	0.272153	60480.04	x	x	x	x	x	x	328.112127	0.154354	5808.6
C_29H_16N+	378.12794	0.567113	13153.26	x	x	x	x	x	x	378.127529	-0.520734	2354.51

C_31H_16N+	402.127582	-0.358362	6719.22	x	x	x	x	x	x	402.127166	-1.393573	2701.61
C_35H_17N+	x	x	x	x	x	x	x	x	x	x	x	x
Alkyl quinoline												
C_10H_10N+	144.080629	-1.021873	24142326.55	144.080616	-1.110334	423310.59	144.080569	-1.433013	273902.78	144.080524	-1.744829	133461.91
C_11H_12N+	158.096255	-1.080069	52827343.08	158.096224	-1.279458	421704.85	158.096178	-1.564611	165386.73	158.096134	-1.843507	83271.5
C_12H_14N+	172.111861	-1.251098	26613194.54	172.111792	-1.651982	121829.29	172.111766	-1.801474	46731.72	172.11172	-2.065575	24902.97
C_13H_16N+	186.127527	-1.066407	5418008.26	186.127531	-1.048067	25548.79	186.127548	-0.956878	13950.27	186.127391	-1.798661	5091.31
Carbazole												
C_12H_10N+	168.080541	-1.398396	7170195.36	168.080529	-1.469047	259392.07	168.080472	-1.8056	54348.5	168.080447	-1.954665	211099.21
C_14H_12N+	194.096259	-0.860822	3360288.61	194.096241	-0.951902	109160.52	194.096164	-1.347776	33342.67	194.096164	-1.349559	70292.22
C_20H_14N+	268.112017	-0.21873	544710.12	268.11197	-0.39349	10818.04	268.111879	-0.732454	6632.36	268.111823	-0.942145	7504.19
C_24H_16N+	318.127737	0.034968	72691.98	x	x	x	x	x	x	318.127507	-0.689765	2980.6
C_30H_20N+	x	x	x	x	x	x	x	x	x	x	x	x



S19 (a)

Injector tip 7

Injector tip 8

N-PAHs

(quinolines and

Fig. S19. Plots of double bond equivalence (DBE) versus carbon number of all CHN_x species in injector tip deposits where x = 1, an annotated plot is given for injector tip 8 showing the discussed compound classes.

S20

(a)

Parent ion	Secondary fragments				
C_13H_14N+	Center Mass (u)	Formula	Mass Deviation (ppm)	Area (intensity)	Neutral loss
	168.080649	C_12H_10N+	-0.753543	42350.3	[M – CH_3H]
	128.061995	C_10H_8+	-0.446183	8561.16	[M – C_2H_5CH]
	105.069934	C_8H_9+	0.541724	14708.87	[M – $C_2H_5C_5$]
	103.054342	C_8H_7+	1.121149	5371.65	[M – $C_2H_5(CH)_2C$]
	94.065323	C_6H_8N+	2.0937	7414.59	[M – $C_2H_5(CH)_5NH$]
	91.054455	C_7H_7+	2.502575	94391.47	[M – $C_2H_5(CH)_2C_2$]
	79.054487	C_6H_7+	3.294923	13590.92	[M – $C_2H_5(CH)_2C_3$]

(b) i.

Parent ion	Secondary fragments				
C_9H_8N+	Center Mass (u)	Assignment	Mass Deviation (ppm)	Area	Neutral loss
(quinoline)	130.064977	C_9H_8N+	-1.146516	22753727.69	-
	128.049307	C_9H_6N+	-1.31343	111593.18	[M-2H]
	115.054166	C_9H_7+	-0.52368	273824.9	[M-NH]
	103.054248	C_8H_7+	0.205877	2627747.6	[M-CHN]
	102.046414	C_8H_6+	0.12502	158144.32	[M-CHN-H]

ii.

Parent ion	Secondary fragments				
C_13H_10N+	Center Mass (u)	Assignment	Mass Deviation (ppm)	Area	Neutral loss
(benzoquinoline)	180.080521	C_13H_10N+	-1.416637	39761353.48	-
	179.072739	C_13H_9N+	-1.180869	2947715.23	[M-H]
	178.06492	C_13H_8N+	-1.157576	2381097.57	[M-2H]
	166.064836	C_12H_8N+	-1.745838	426220.3	[M-CH-H]
	165.069597	C_13H_9+	-1.695639	673475.05	[M-NH]
	154.064831	C_11H_8N+	-1.911554	952140.22	[M-$(CH)_2$]
	141.057028	C_10H_7N+	-1.930894	70410.56	[M-$(CH)_3$]
	140.049225	C_10H_6N+	-1.789625	61834.59	[M-$(CH)_3H$]
	128.049302	C_9H_6N+	-1.357261	196864.25	[M-$(CH)_4$]
	108.080729	C_7H_10N+	-0.436517	391838.41	[M-C_6]
	107.072909	C_7H_9N+	-0.389194	33473.97	[M-C_6H]
	106.065114	C_7H_8N+	-0.108234	27742.09	[M-$(CH)_2C_4$]
	104.049475	C_7H_6N+	-0.003724	14044.94	[M-$(CH)_4C_2$]

	103.054259	C_8H_7+	0.311792	18846.28	[M-CHN(CH)$_2$C$_2$]
	94.065249	C_6H_8N+	1.309504	34306.33	[M-(CH)$_2$C$_5$]
	93.057445	C_6H_7N+	1.547004	13517.84	[M-(CH)$_3$C$_4$]
	91.054397	C_7H_7+	1.868241	13236.98	[M-CHN(CH)$_2$C$_3$]
	80.049744	C_5H_6N+	3.353475	13841.34	[M-(CH)$_4$C$_4$]

(c) i.

Parent ion	**Secondary fragments**				
C_12H_10N+					
(carbazole)	Center Mass (u)	Assignment	Mass Deviation (ppm)	Area	Neutral loss
	168.080359	C_12H_10N+	-2.479035	33951001.41	-
	167.072717	C_12H_9N+	-1.398117	42841238.99	[M-H]
	154.064838	C_11H_8N+	-1.864652	1127552.75	[M-(CH)H]
	152.061783	C_12H_8+	-1.770072	593252.96	[M-(NH)H]
	141.069614	C_11H_9+	-1.863438	4536790.34	[M-(CHN)]
	140.061805	C_11H_8+	-1.760533	2135647.44	[M-(CHN)H]
	139.054009	C_11H_7+	-1.561679	2952800.74	[M-(CHN)(2H)]
	115.054171	C_9H_7+	-0.480103	2342975.15	[M-(CHN)(CH)$_2$]
	89.038754	C_7H_5+	1.990212	201976.81	[M-(CHN)(CH)$_4$]

ii.

Parent ion	**Secondary fragments**				
C_16H_11N+	Center Mass (u)	Assignment	Mass Deviation (ppm)	Area	Neutral loss
(benzocarbzole)	217.08849	C_16H_11N+	-0.50958	98725.94	-
	165.069562	C_13H_9+	-1.905951	138381.59	[M-CHN(CH)C]
	176.061741	C_14H_8+	-1.765407	64654.65	[M-CHN(CH)H]
	177.056975	C_13H_7N+	-1.836766	43261.27	[M-(CH)$_3$H]
	166.06483	C_12H_8N+	-1.779945	15965.32	[M-(CH)$_3$C]
	163.053874	C_13H_7+	-2.164471	521241.66	[M-CHN(CH)$_2$H]
	152.061752	C_12H_8+	-1.974013	62202.34	[M-CHN(CH)$_2$C]
	150.046148	C_12H_6+	-1.68757	47538.7	[M-CHN(CH)$_3$H]
	140.049209	C_10H_6N+	-1.903593	64042.88	[M-(CH)$_5$C]
	139.053962	C_11H_7+	-1.90445	95349.13	[M-CHN(CH)$_3$C]
	128.061867	C_10H_8+	-1.444762	20497.63	[M-CHN(CH)$_2$C$_3$]

(d) i.

C_10H_10N+	Center Mass (u)	Assignment	Mass Deviation (ppm)	Area	Neutral loss
	144.080517	C_10H_10N+	-1.794899	14582916	-
	129.05711	C_9H_7N+	-1.479692	21409.31	[M-CH$_3$]
	130.064906	C_9H_8N+	-1.690158	807.16	[M-CH$_2$]
	129.069671	C_10H_9+	-1.592923	55590.72	[M-H]
	128.049278	C_9H_6N+	-1.540934	33959.2	[M-CH$_4$]
	117.069773	C_9H_9+	-0.885944	402844.14	[M-CH$_4$]
	116.049395	C_8H_6N+	-0.690452	219164.96	[M-C$_2$H$_4$]
	115.054158	C_9H_7+	-0.593446	448145.25	[M-CH$_3$]
	103.054231	C_8H_7+	0.041763	131747.92	[M-C$_2$H$_3$]

ii.

Parent ion	Secondary fragments				
C_11H_12N+	Center Mass (u)	Assignment	Mass Deviation (ppm)	Area	Neutral loss
	158.096181	C_11H_12N+	-1.547651	11802842.12	-
	143.072753	C_10H_9N+	-1.380619	2882915.86	[M-CH_3]
	130.064992	C_9H_8N+	-1.025907	1547264.03	[M-C_2H_4]

Fig. S20. MS/MS fragmentation data of different aromatic nitrogen moieties highlighted in **Table 1** in the main text. **(a)** alkyl phenyl pyridine, $C_{13}H_{14}N^+$, **(b)** quinolines i. $C_9H_8N^+$, ii. $C_{13}H_{10}N^+$. **(c)** carbazoles i. $C_{12}H_{10}N^+$, ii. $C_{16}H_{11}N^+$. **(d)** alkylated quinolines **i.** $C_{10}H_{10}N^+$, ii. $C_{11}H_{12}N^+$.

S21

(a) i. DHB matrix

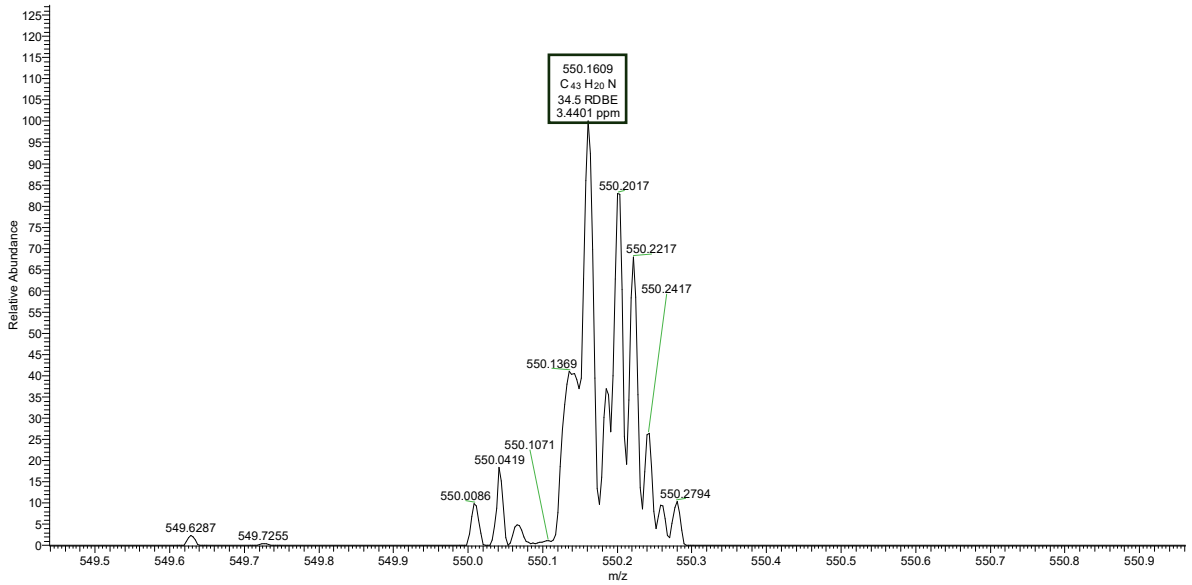
Compound class	Max. mass ion			
	3D OrbiSIMS	AP- MALDI repeat 1	AP-MALDI repeat 2	AP-MALDI repeat 3
Benzoquinoline	$C_{35}H_{18}N^+$ (-0.6 ppm)	$C_{25}H_{14}N^+$ (5.955 ppm)	$C_{25}H_{14}N^+$ (1.353 ppm)	$C_{25}H_{14}N^+$ (3.578 ppm)
Alkyl phenyl pyridine	$C_{59}H_{106}N^+$ (-1.1 ppm)	$C_{50}H_{88}N^+$ (-2.49 ppm)	$C_{22}H_{32}N^+$ (4.09 ppm)	$C_{55}H_{98}N^+$ (-2.37 ppm)
Carbazole	$C_{28}H_{18}N^+$ (-0.8 ppm)	$C_{28}H_{18}N^+$ (3.28 ppm)	$C_{26}H_{18}N$+ (1.63 ppm)	$C_{26}H_{18}N$+ (4.29 ppm)
Alkyl quinoline	$C_{43}H_{76}N^+$ (-0.5 ppm)	$C_{46}H_{82}N^+$ (-1.23 ppm)	$C_{20}H_{30}N^+$ (4.78 ppm)	$C_{46}H_{82}N^+$ (4.78 ppm)

ii. TCNQ matrix

Compound class	Max. mass ion			
	3D OrbiSIMS	AP-MALDI repeat 1	AP-MALDI repeat 2	AP-MALDI repeat 3
Benzoquinoline	$C_{35}H_{18}N^+$ (-0.6 ppm)	$C_{45}H_{22}N^+$ (5.955 ppm)	$C_{43}H_{20}N^+$ (3.598 ppm)	$C_{45}H_{22}N^+$ (4.54 ppm)
Alkyl phenyl pyridine	$C_{59}H_{106}N^+$ (-1.1 ppm)	$C_{30}H_{48}N^+$ (5.89 ppm)	$C_{29}H_{46}N^+$ (4.88 ppm)	$C_{29}H_{46}N^+$ (4.54 ppm)
Carbazole	$C_{28}H_{18}N^+$ (-0.8 ppm)	$C_{28}H_{18}N^+$ (-3.4 ppm)	$C_{28}H_{18}N$+ (-1.86 ppm)	$C_{28}H_{18}N$+ (-1.86 ppm)
Alkyl quinoline	$C_{43}H_{76}N^+$ (-0.5 ppm)	$C_{31}H_{52}N^+$ (3.17 ppm)	$C_{28}H_{46}N^+$ (4.45 ppm)	$C_{27}H_{44}N^+$ (6.1 ppm)

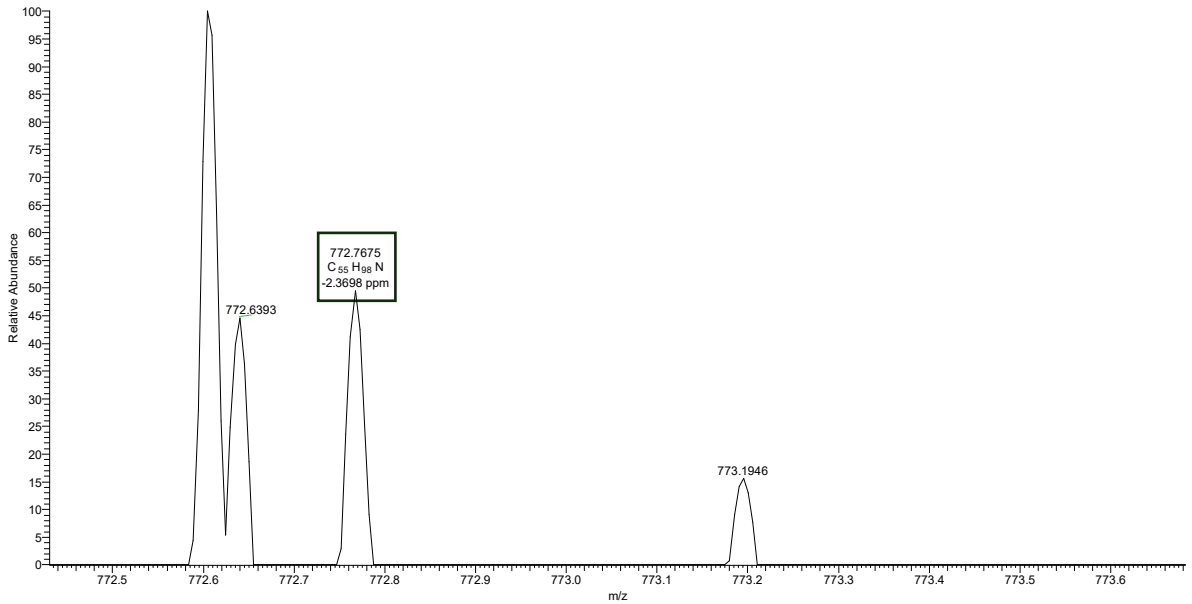
(b) i. Benzoquinolines

159+TCNQ13%(1) #6-225 RT: 0.09-1.43 AV: 220 NL: 5.42E2
T: FTMS + p MALDI Full ms [150.0000-1500.0000]

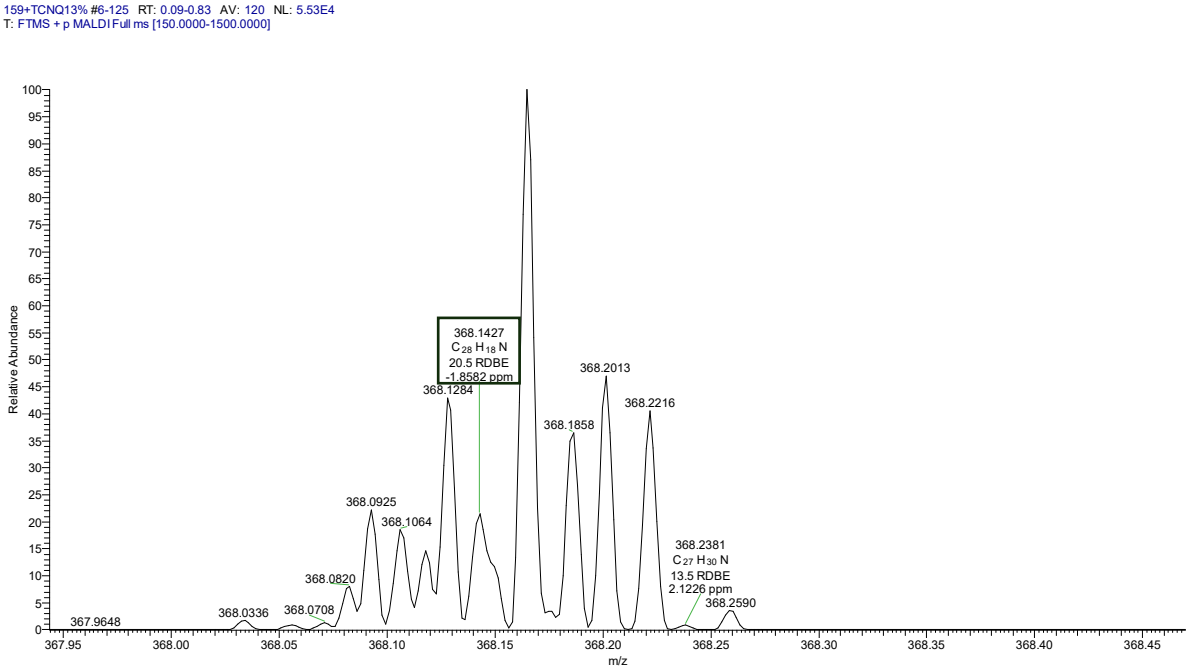


ii. Alkyl phenyl pyridines

cokeTHFDBE3 #2-34 RT: 0.02-0.35 AV: 33 NL: 2.01E1
T: FTMS + p MALDI Full ms [150.0000-2000.0000]



iii. Carbazoles



iv. Alkylated quinolines

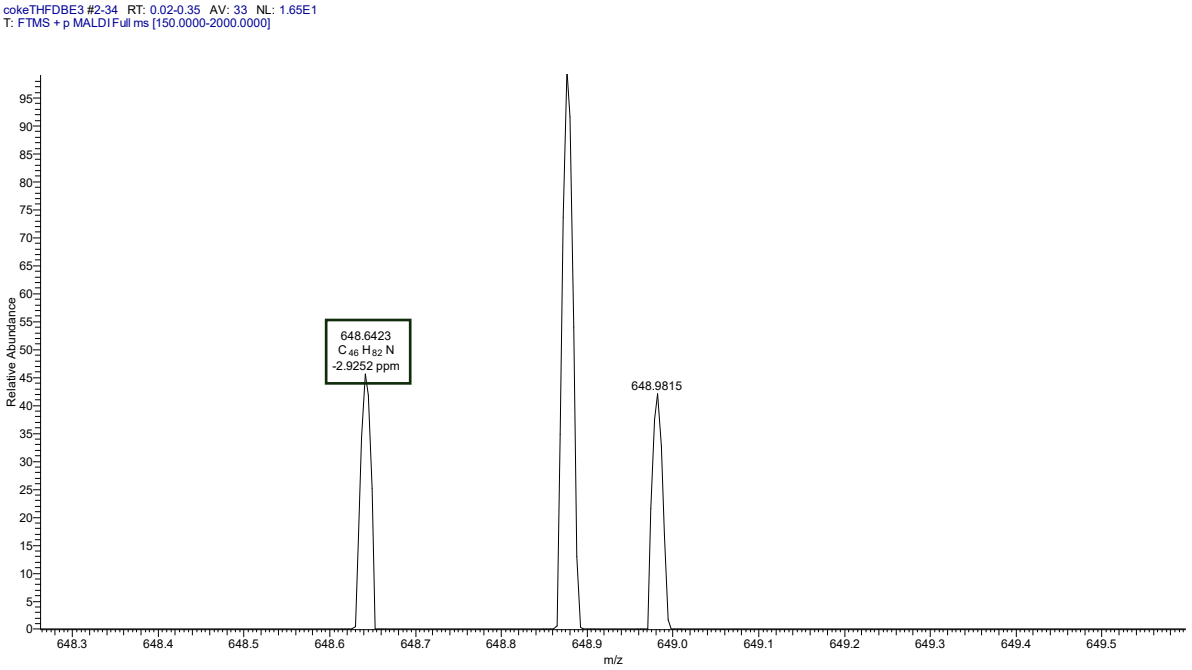
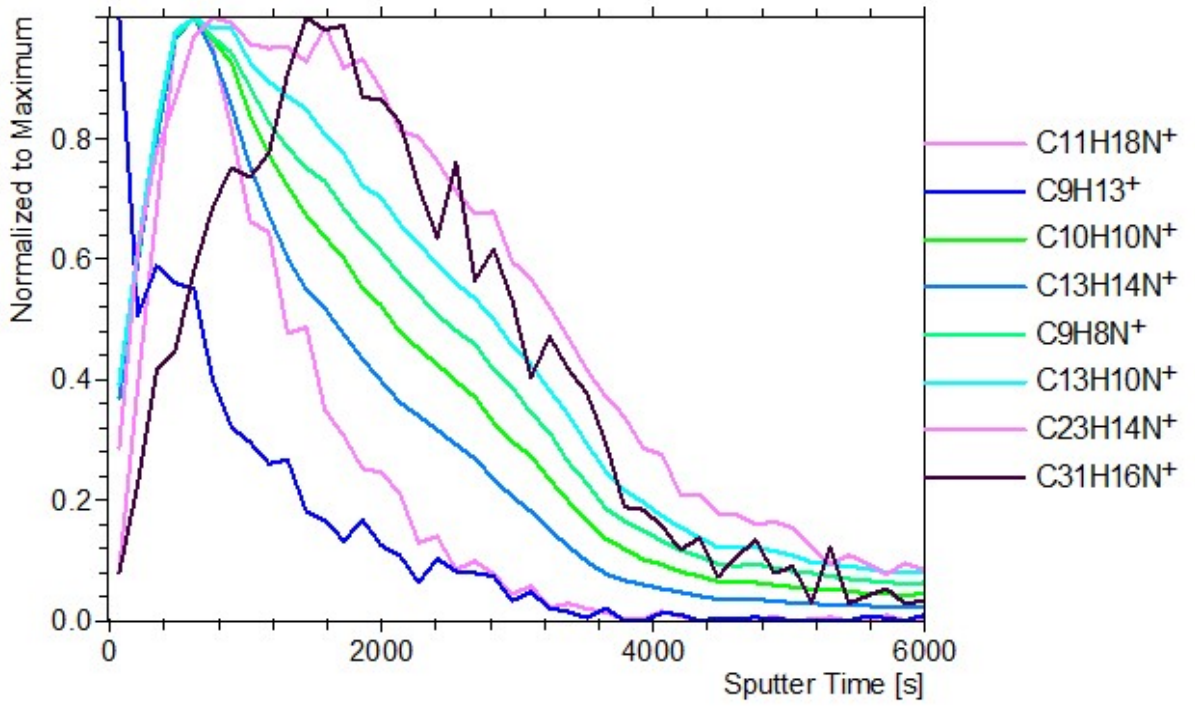


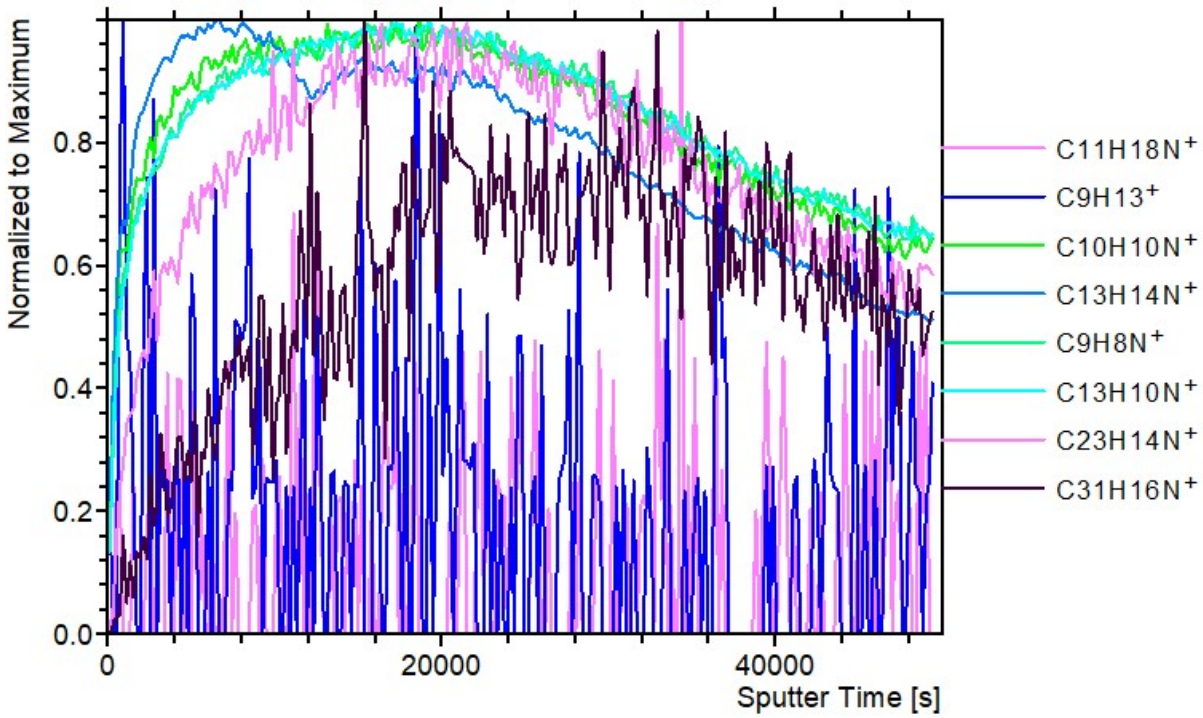
Fig. S21. (a) Table of maximum mass ions for each compound class annotated in the 3D OrbiSIMS and AP-MALDI MS repeat spectra from injector tip 5. **(b)** Raw AP-MALDI spectra using a TCNQ matrix showing peaks for maximum mass ions of each compound class from 'AP-MALDI dataset 2'.

S22

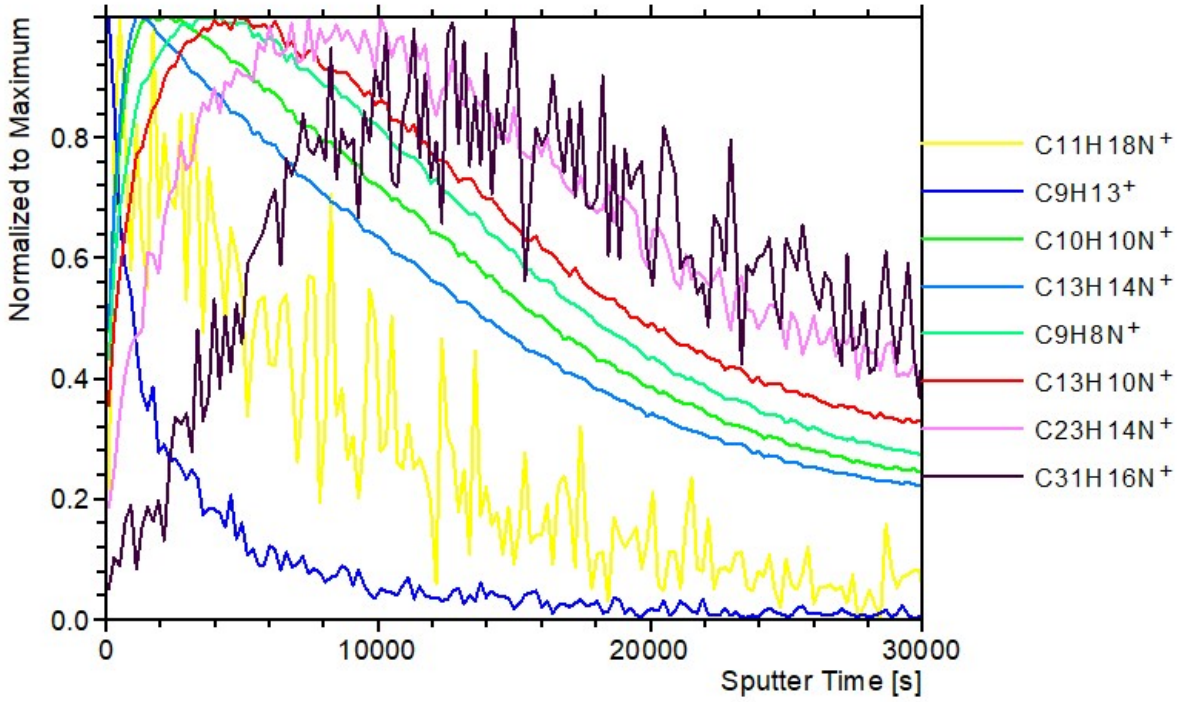
Injector tip 1



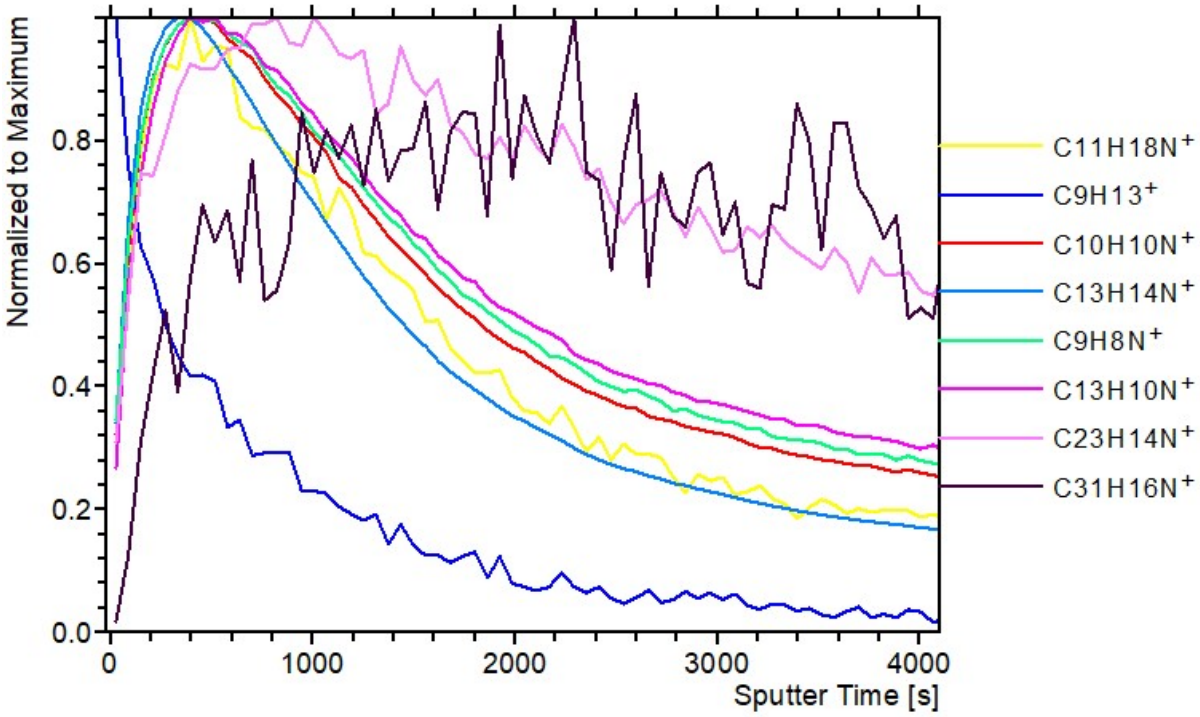
Injector tip 3



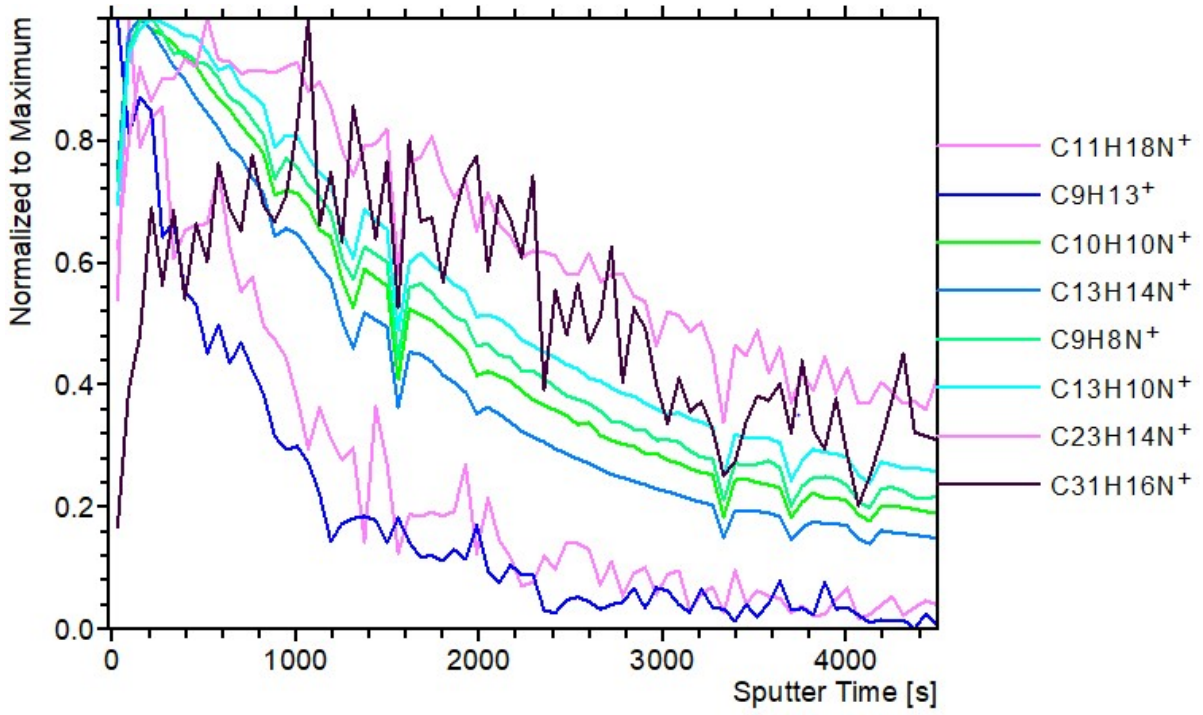
Injector tip 4



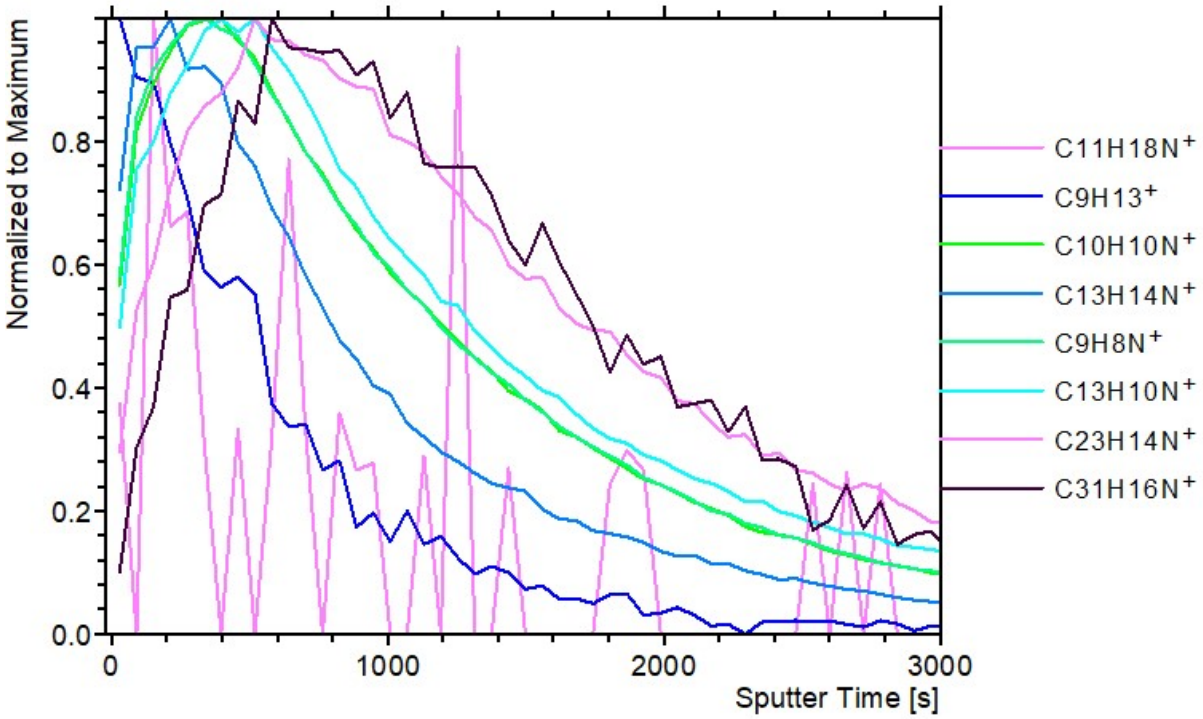
Injector tip 5



Injector tip 6



Injector tip 7



Injector tip 8

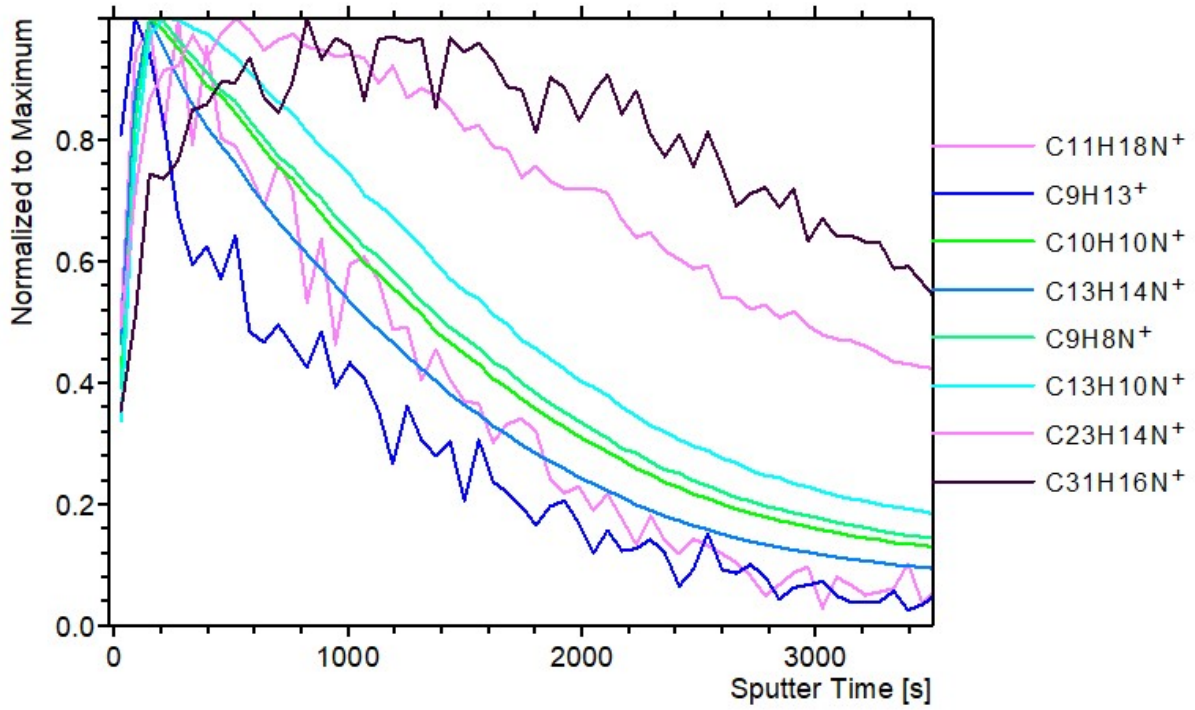
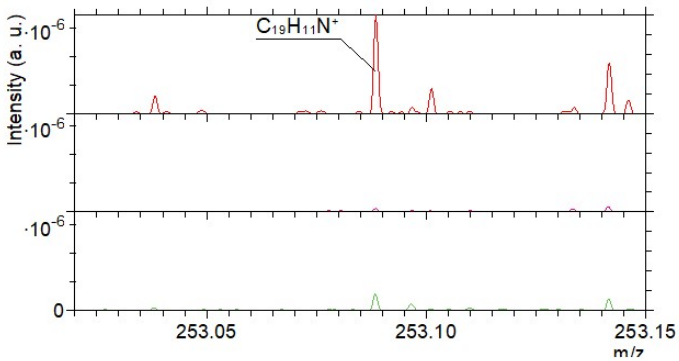


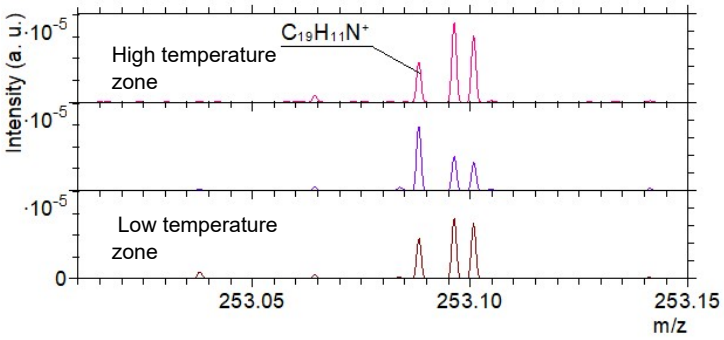
Fig. S22. 3D OrbiSIMS depth profiles of the highlighted nitrogen aromatic species in **Fig. 2** in the main text for all injector tip deposits ions displayed are (in order of prevalence at depth).

S23

(a)



(b)



(c)

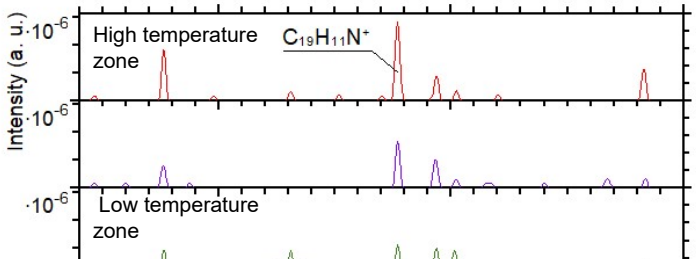


Fig. S23. 3D OrbiSIMS spectra (normalized to total ion counts) of benzoquinoline ($C_{19}H_{11}N^+$) taken from different positions along (a) injector needle 1, (b) injector needle 2 and (c) injector needle 3.

S24

(a)

C_7H_5O_3-	Centre Mass (u)	Assignment	Mass Deviation (ppm)	Area
	109.029453	C_6H_5O_2-	-0.459667	14619.49
	93.034421	C_6H_5O-	-1.799719	19606.87

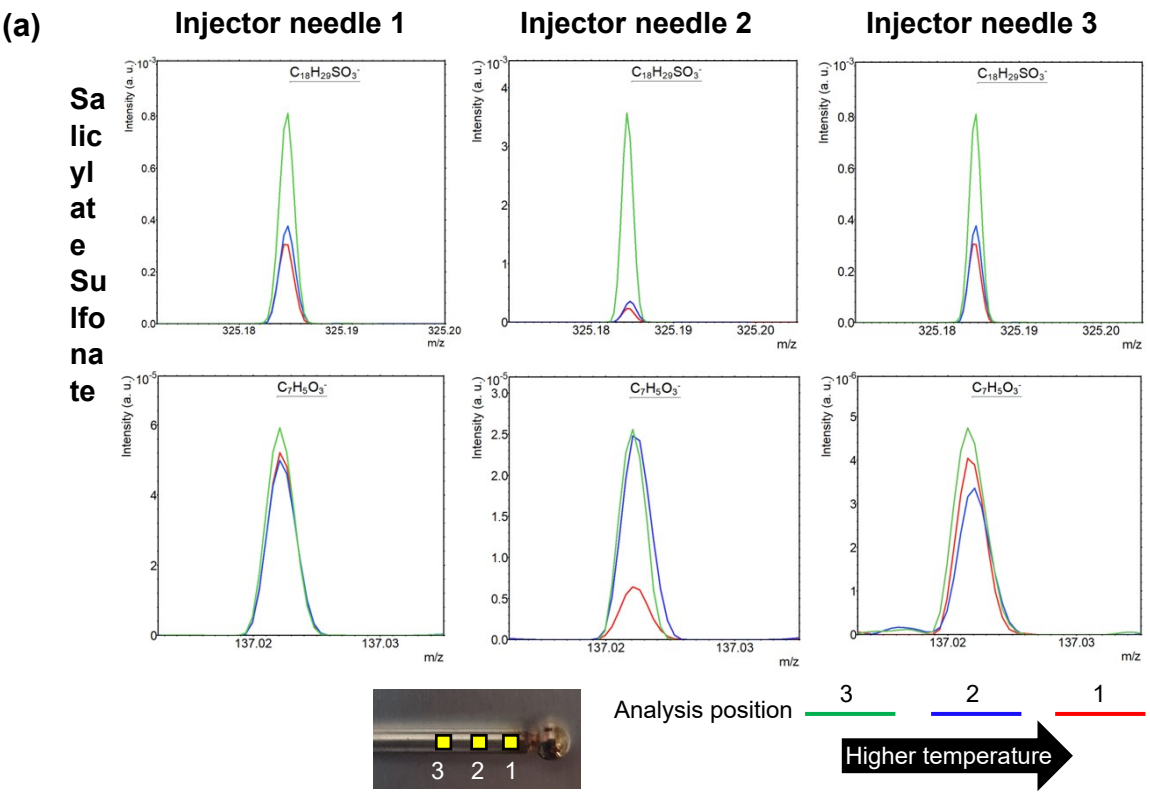
(b)

C_8H_7O_3-	Centre Mass (u)	Assignment	Mass Deviation (ppm)	Area
	151.040012	C_8H_7O_3-	-0.36559	71818.67
	107.050281	C_7H_7O-	0.394903	45007.94
	122.037346	C_7H_6O_2-	0.150098	4178.69
	123.045164	C_7H_7O_2-	0.0883	8377.24
	123.008824	C_6H_3O_3-	0.456591	1634.14
	109.029552	C_6H_5O_2-	0.447403	1737.25

(c)

C_11H_7O_3-	Centre Mass (u)	Assignment	Mass Deviation (ppm)	Area
	187.040068	C_11H_7O_3-	0.001186	111752.82
	159.045115	C_10H_7O_2-	-0.237498	47219.63
	143.050163	C_10H_7O-	-0.530103	11727.89

Fig. S24. MS/MS fragmentation for different salicylate types. **(a)** $C_7H_5O_3^-$ (with no alkyl chain), **(b)** $C_8H_7O_3^-$ (with alkyl chain length of 1). **(c)** $C_{11}H_7O_3^-$ (benzene fused salicylate).



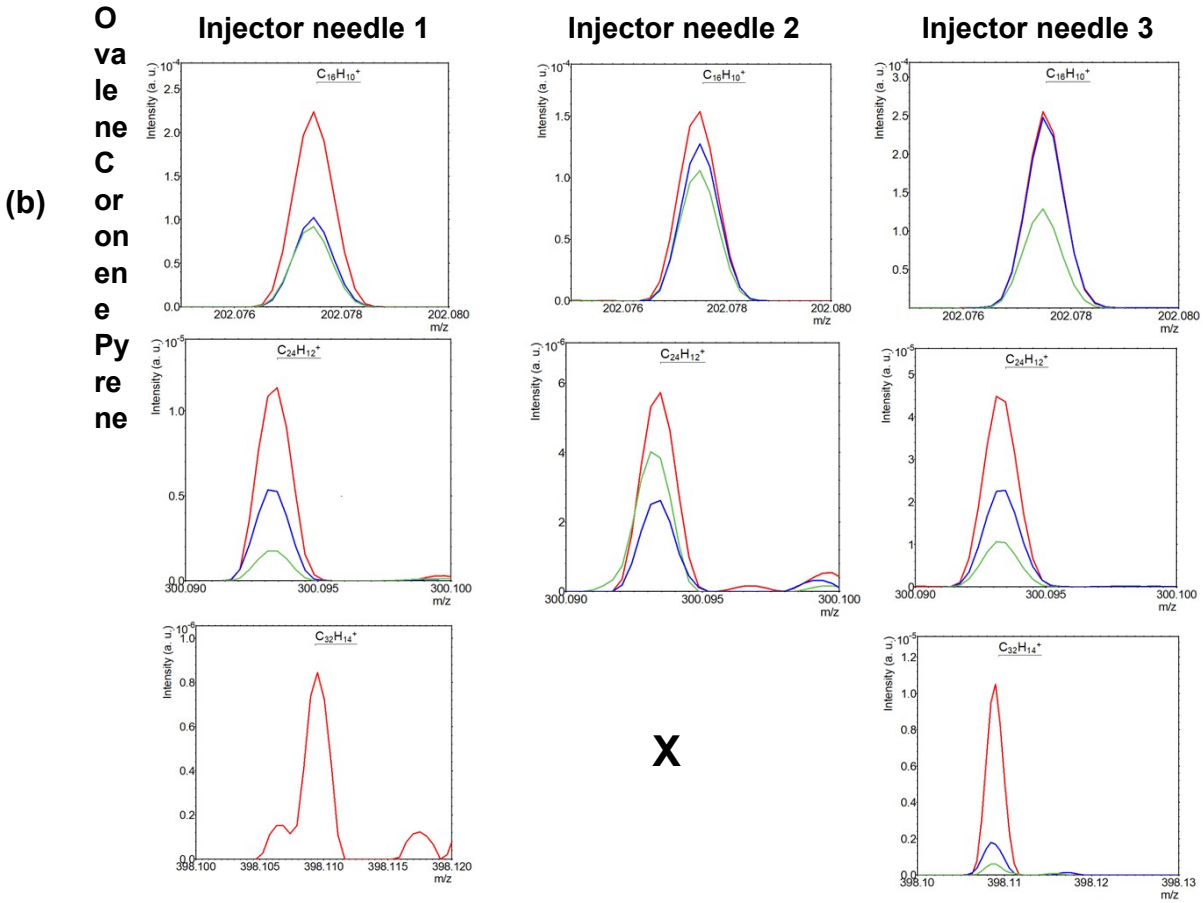


Fig. S25. Normalized spectral comparison of three different positions on injector needles 1, 2 and 3. **(a)** sulfonates and salicylates, **(b)** PAHs.

Supplementary references:

1. ASTM D4814 - 21 - Standard Specification for Automotive Spark-Ignition Engine Fuel.

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