

Supplemental Information for

**Visualizing Mass Transport in Desorption Electrospray Ionization using Time-of-Flight
Secondary Ion Mass Spectrometry: A Look at the Geometrical Configuration of the Spray**

Shin Muramoto

National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
1-301-975-5997 (phone)
1-301-417-1321 (fax)
shinichiro.muramoto@nist.gov

Table S-1. DESI-MS intensity of cocaine as a function of incidence angle, where the angle varied from 20 to 75 in 5 intervals. Data was acquired over (1, 3, and 5) min durations, and counts were integrated between m/z 303 and m/z 305. The geometrical configurations of the DESI spray were a probe distance of 3 mm and a tip height of 1 mm. All other parameters were as described in the Experiment section.

Incidence Angle	Acquisition Time		
	1 min ($\times 10^7$ counts)	3 min ($\times 10^7$ counts)	5 min ($\times 10^7$ counts)
20°	11	38	54
	3.8	23	41
	15	18	39
	9.1	29	46
	2.1	43	61
25°	6.1	22	37
	6.6	15	18
	7.0	9.0	13
	6.4	27	41
	5.7	21	33
30°	3.5	9.5	15
	3.7	10	19
	2.8	7.5	13
	3.5	9.4	18
	2.1	6.5	16
35°	2.1	5.0	7.7
	1.0	4.2	5.8
	2.3	4.3	7.3
	1.3	3.7	5.2
	1.5	4.9	6.3
40°	0.95	2.2	2.8
	0.79	1.9	2.5
	0.91	2.6	2.4
	0.78	2.2	2.9
	0.75	1.8	2.3
45°	0.71	1.1	1.4
	0.54	1.2	1.5
	0.55	1.5	1.8
	0.68	1.0	1.3
	0.65	1.2	1.6
50°	0.43	0.86	1.2
	0.24	0.74	0.96
	0.28	0.81	0.83
	0.34	0.83	1.1
	0.39	0.85	9.8
55°	0.17	0.57	0.61
	0.16	0.28	0.35

	0.13 0.17 0.16	0.55 0.56 0.46	0.56 0.59 0.50
60°	0.099 0.10 0.089 0.095 0.094	0.29 0.36 0.34 0.3 0.32	0.5 0.52 0.53 0.51 0.49
65°	0.13 0.13 0.099 0.12 0.10	0.28 0.24 0.21 0.23 0.23	0.4 0.36 0.38 0.4 0.38
70°	0.16 0.07 0.09 0.13 0.12	0.28 0.23 0.25 0.26 0.18	0.4 0.36 0.29 0.35 0.37
75°	0.009 0.069 0.006 0.024 0.010	0.13 2.3 0.45 0.38 1.6	0.20 4.1 0.65 0.98 2.6

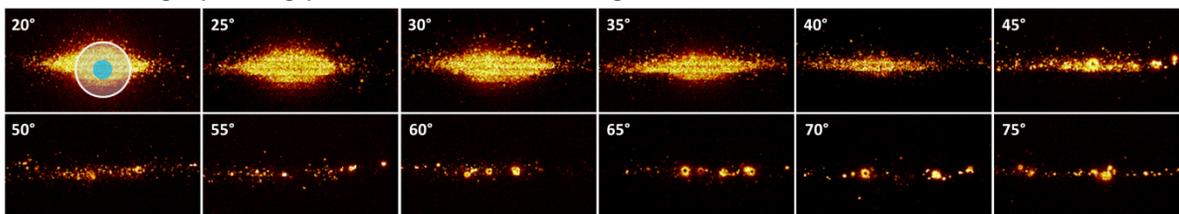
Table S-2. The dimensions of the *lateral* dispersion lengths of the secondary droplet plume on the silicon collection substrate at incidence angles of 30°, 45°, 60°, and 75° at probe distances of (3, 5, 7, 9, and 11) mm, and at tip heights of (1, 2, and 3) mm.

<i>Lateral</i> Dispersion Length (mm)					
Tip Height	Probe Distance	30°	45°	60°	75°
1 mm	3 mm	5.7 ± 0.1	5.1 ± 0.1	5.8 ± 0.6	7.6 ± 0.9
	5 mm	7.7 ± 1.1	5.3 ± 0.6	6.6 ± 0.9	6.5 ± 1.1
	7 mm	8.3 ± 0.8	6.4 ± 0.7	4.5 ± 0.8	4.9 ± 0.3
	9 mm	9.9 ± 1.0	7.7 ± 0.7	-	-
	11 mm	11.7 ± 0.7	6.6 ± 0.2	-	-
2 mm	3 mm	5.4 ± 0.6	5.5 ± 0.6	7.3 ± 0.7	10.0 ± 0.3
	5 mm	7.7 ± 0.1	7.7 ± 0.3	9.5 ± 0.7	7.0 ± 0.1
	7 mm	9.0 ± 0.4	10.7 ± 0.8	9.9 ± 0.8	5.1 ± 0.4
	9 mm	10.0 ± 0.7	11.9 ± 2.7	9.5 ± 1.1	-
	11 mm	11.3 ± 0.1	12.1 ± 0.4	2.9 ± 1.4	-
3 mm	3 mm	7.2 ± 0.1	6.7 ± 0.1	9.5 ± 0.1	9.3 ± 0.5
	5 mm	8.7 ± 0.3	9.9 ± 0.2	11.3 ± 0.3	7.3 ± 0.3
	7 mm	9.8 ± 1.3	11.0 ± 0.4	13.1 ± 1.0	5.8 ± 1.1
	9 mm	11.0 ± 0.4	13.3 ± 0.7	10.9 ± 1.3	-
	11 mm	11.3 ± 0.3	14.2 ± 0.3	10.9 ± 1.5	-

Table S-3. The dimensions of the *vertical* dispersion lengths of the secondary droplet plume on the silicon collection substrate at incidence angles of 30°, 45°, 60°, and 75° at probe distances of (3, 5, 7, 9, and 11) mm, and at tip heights of (1, 2, and 3) mm.

<i>Vertical</i> Dispersion Length (mm)					
Tip Height	Probe Distance	30°	45°	60°	75°
1 mm	3 mm	1.9 ± 0.1	0.8 ± 0.2	0.5 ± 0.0	0.5 ± 0.1
	5 mm	1.5 ± 0.2	0.9 ± 0.2	0.7 ± 0.1	0.5 ± 0.1
	7 mm	1.4 ± 0.1	1.1 ± 0.0	1.0 ± 0.1	0.5 ± 0.0
	9 mm	1.4 ± 0.2	1.2 ± 0.1	-	-
	11 mm	1.5 ± 0.3	1.2 ± 0.1	-	-
2 mm	3 mm	2.0 ± 0.1	1.4 ± 0.1	0.9 ± 0.1	0.6 ± 0.1
	5 mm	2.5 ± 0.1	1.9 ± 0.1	1.0 ± 0.0	0.7 ± 0.1
	7 mm	3.0 ± 0.0	2.2 ± 0.1	1.6 ± 0.0	0.8 ± 0.0
	9 mm	3.5 ± 0.4	2.6 ± 0.4	1.4 ± 0.1	-
	11 mm	4.3 ± 0.7	2.9 ± 0.5	0.9 ± 0.1	-
3 mm	3 mm	2.0 ± 0.0	1.5 ± 0.1	1.2 ± 0.3	1.0 ± 0.1
	5 mm	2.4 ± 0.2	2.3 ± 0.2	1.6 ± 0.2	0.9 ± 0.1
	7 mm	3.4 ± 0.2	3.3 ± 0.2	2.0 ± 0.2	0.8 ± 0.1
	9 mm	4.0 ± 0.4	3.6 ± 0.3	1.9 ± 0.1	-
	11 mm	4.5 ± 0.3	3.9 ± 0.2	1.4 ± 0.1	-

(a) Collector Ion Images (no voltage) – as a function of incidence angle



(b) Collector Ion Images (+ 4000 V) – as a function of incidence angle

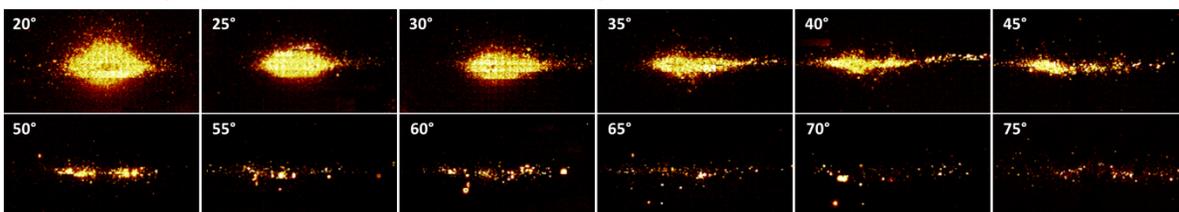
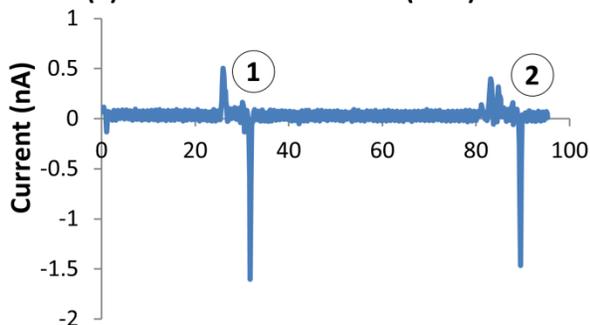


Figure S-1. ToF-SIMS ion images of the collectors showing the change in the desorption profile (spatial distribution) of analyte as a function of incidence angle (14 mm × 7 mm image size), captured at a probe distance of 3 mm and at a tip height of 1 mm. The collector was exposed to the DESI spray for 10 s. For this collection experiment, the DESI probe was held at a potential of (a) 0 kV and (b) + 4000 V and the collector substrate was grounded for (a) and held at + 500 V for (b), which is the potential used for the MS inlet tube during a normal ambient MS analysis.

(a) Current Measurement (0 kV)



(b) Current Measurement (4 kV)

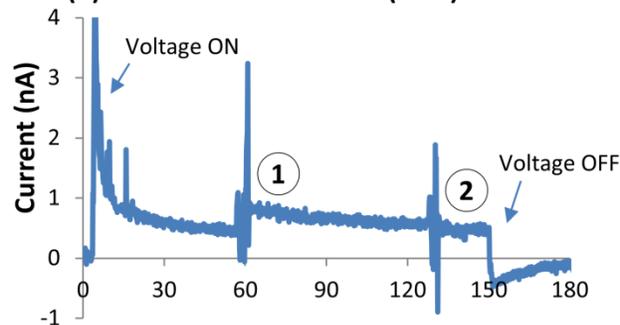


Figure S-2. Current versus time plots showing the measured current of the secondary droplets with (a) no applied potential and with (b) 4 kV applied potential. (1) refers to the point at which the Teflon well with 200 ng of deposited cocaine was exposed to the DESI spray, and (2) refers to the point at which a blank Teflon well was exposed to the spray. All measurements started on a blank Teflon well. The aluminum electrode connected to a picoammeter was placed approximately 10 mm from the impact point of the DESI spray. The pneumatic assist gas pressure was 80 psi, flow rate was 5 $\mu\text{L}/\text{min}$, and incidence angle was 30° to maximize analyte transfer.

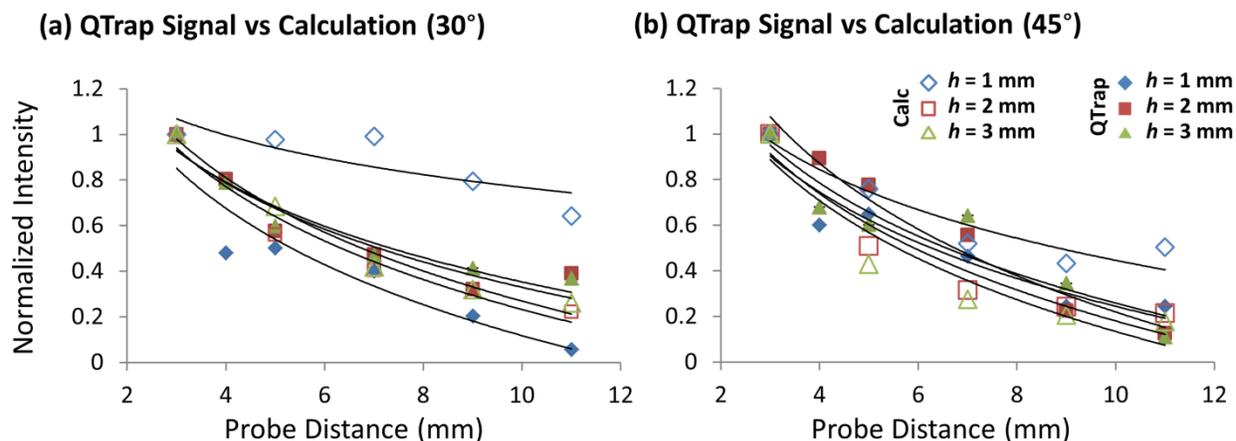


Figure S-3. Relative QTrap (ambient MS) intensities of the analyte plotted as a function of probe distance at incidence angles of 30° and 45° at tip heights of (1, 2, and 3) mm (solid markers), and relative intensities calculated based on the area of the inlet orifice divided by the area of the desorption profile for incidence angles of 30° and 45° at tip heights of (1, 2, and 3) mm. The trends show that for these incidence angles, the ambient MS intensities are proportional to the fraction of the secondary droplet plume that overlaps with the MS inlet orifice. Probe distance here refers to the distance between the DESI impact point and the tip of the inlet capillary. Intensities for incidence angles of 60° and 75° could not be calculated due to difficulties in measuring the area of the desorption profile.