Supporting information

Enabling Quantitative Analysis for Ambient Ionization Mass Spectrometry: Development of Internal Standard Coated Capillary Sampler

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1. Fabrication of sampling capillary of different volumes.

A series of sampling capillary is fabricated with capillaries of different lengths. Each consists of a capillary for liquid transfer, a pipette tip as the holder, and a plastic bulb.

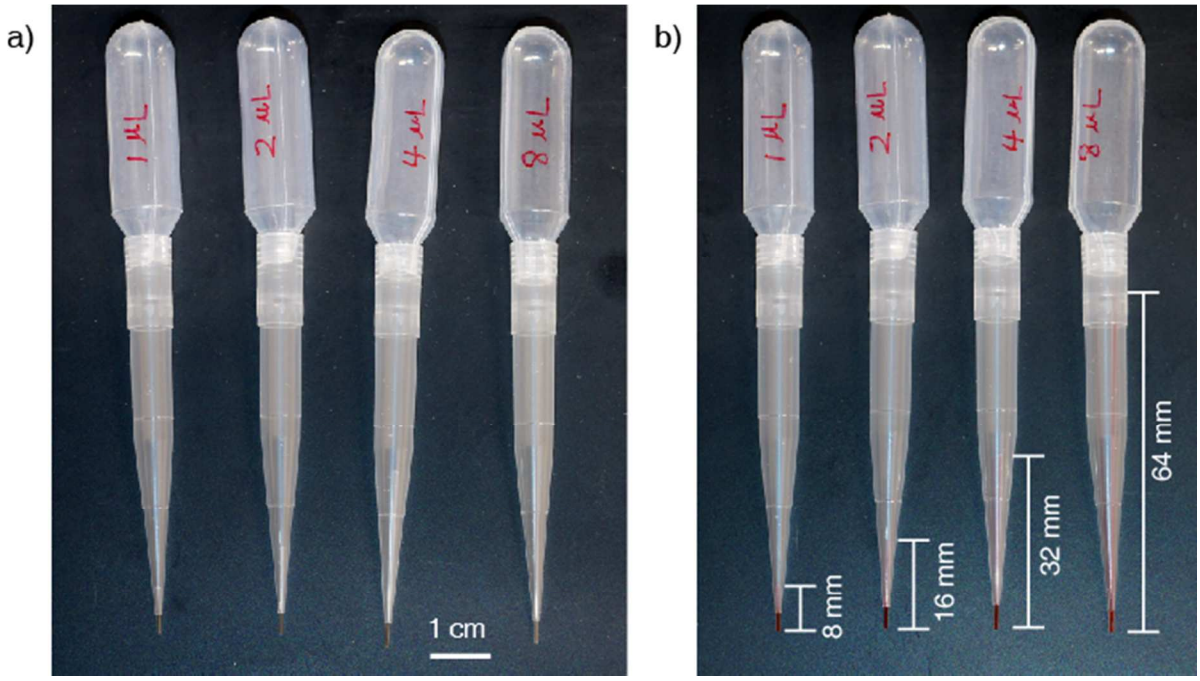

Fig. S-1 a) Sampling capillaries with different sampling volumes (from left to right, 1, 2, 4, 8 μL). b) Blood samples are collected in the sampling capillaries. The length of each capillary is noted.

2. Characterization on the drying coating of internal standard.

Table S-1. Drying time for coating the capillary using methanol solution containing internal standard; oven temperature, 60 °C.

	For methanol			
Volume (μL)	1	2	4	8
Drying time (s)	106 ± 3	211 ± 3	310 ± 8	796 ± 58

3. Quantitative analysis using capillary samplers with paper spray, LTP and DESI.

Table S-2. Capillary sampler for quantitative analysis using ambient ionization methods of paper spray, LTP and DESI.

Analysis[a,b]	**Analyte Con. (ng/mL)**	**Mean analyte/IS**	**Standard deviation**	**Relative standard deviation (%)**
Paper Spray MS analysis of imatinib in blood TSQ (IS: imatinib-d8) (n≥3)	4000	39.2	1.2	3.1
	2000	19.7	0.70	3.6
	1000	9.8	0.31	3.2
	500	5.0	0.12	2.4
	250	2.6	0.070	2.7
	130	1.2	0.046	3.8
	63	0.64	0.019	3.0
	30	0.31	0.010	3.2
	10	0.11	0.003	2.7
LTP MS analysis of atrazine in river water Orbitrap IS: atrazine-d5 (n=5)	500	4.79	0.23	4.8
	100	0.91	0.025	2.7
	40	0.37	0.012	3.2
	10	0.08	0.006	7.5
DESI MS Analysis of cocaine in urine Orbitrap IS: cocaine-d3 (n=5)	1000	9.59	0.23	2.4
	180	1.76	0.034	1.9
	80	0.84	0.016	1.9
	30	0.31	0.010	3.2

[a]1 μL capillary sampler used.

[b]100 ng/mL concentration of internal standard in methanol solution for IS coating.

4. Characterization of capillary samplers.

Table S-3. Sample collection time and dispensing time (onto paper) for different liquids using capillary action.

	Urine	**Methanol**	**Blood**				**Serum**			
Viscosity (mPa·s, 20 °C)	0.8	0.59	~10, 3-4 (37 °C)				1.4-1.8			
Surface tension (mN/m, 20 °C)	~66	22.6	~61, ~58 (37 °C)				~59, ~53 (37 °C)			
Volume (μL)	8	8	8	4	2	1	8	4	2	1
Loading time (s)	1.0±0.1	1.2±0.1	15.4±0.8	3.8±0.3	1.2±0.1	<0.5	1.0±0.1	<0.5	<0.5	<0.5
Dispensing time (s)	13.8±0.6	6.4±0.3	>10s; ~2s, pressurized				11.2±0.7	4.9±0.7	2.7±0.1	1.2±0.1

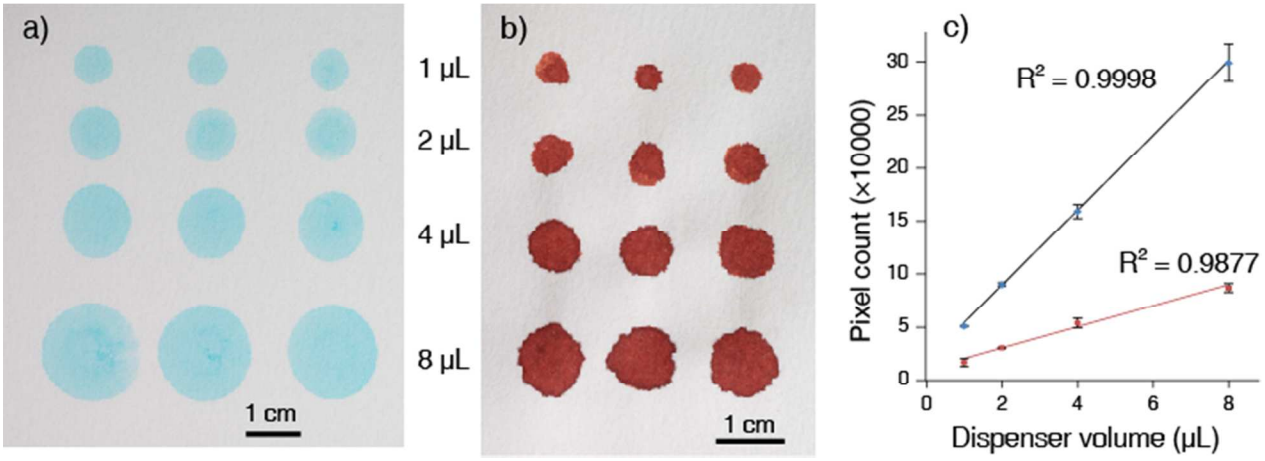

Fig. S-2 a) Liquid samples with low viscosity (methanol solution, urine, serum) could be dispensed on paper using only capillary action. Array of samples prepared with haematoxylin dye in methanol solution (10 mg/L) were prepared with the dispensers. b) Blood was transferred onto chromatography paper (0.18 mm thick) to form array of DBSs of different sizes. c) Area of sample spot (pixel count obtained with Photoshop, Adobe, Inc) in b) vs. capillary volume.