Supporting Information

Online hyphenation of in-capillary aptamer-functionalized solid-phase microextraction and extraction nanoelectrospray ionization for miniature mass spectrometry analysis

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Table S1. The amount of the caffeine-specific aptamers immobilized on the aluminum foil SPME strip with different gold-sputtering time.

Sputtering time (s)	20	40	60	80	100	120
UV Absorbance at 260 nm	0.704	0.379	0.390	0.394	0.450	0.456
Immobilization amount ($nmol/cm^2$)	0.109	0.812	0.789	0.780	0.659	0.645

Table S2. Instrumental parameters of the miniature mass spectrometer.

Mode	Polarity	Spray voltage (kV)	DAPI injection size (ms)	CID amplitude (V)	Mass range (*m/z*)
Full-scan	Positive	2.8	40	/	50–300
MS/MS	Positive	2.8	50	1.2	50–220

Table S3. Results of recovery experiments spiked at low, medium, and high concentration levels (n = 6).

Sample	Amount spiked (ng/mL)	Amount detected (ng/mL)	Recovery (%)	RSD (%)
Electronic cigarette liquid	20	22.3	111.5	3.1
	50	46.2	92.4	4.6
	100	89.3	89.3	5.2
Beverage	20	21.7	108.5	3.8
	50	44.6	89.2	5.3
	100	87.5	87.5	6.1

Table S4. Comparison of the current method with other approaches for the analysis of caffeine.

Matrix	Sample preparation	Analytical Technique	Analysis time (min)	LOD (μg/mL)	LOQ (μg/mL)	Linear range (μg/mL)	RSD (%)	Reference
Tea, coffee, and beverage	DLLME	GC–NPD	~31	0.02	0.05	0.05–500	3.2	[1]
Tea	MIP-SPE	ESI-IMS	154	0.20	0.50	0.5–20	< 6.0	[2]
Coffee	DES-LPME	HPLC-UV	8	0.12	0.40	0.5–100	2.2	[3]
Beverage	DLLME	UV–Vis	960	0.46	1.54	2–75	2.1	[4]
Beverage	DDSME	GC–MS	12	0.004	0.05	0.05–5	4.4	[5]
Beverage and pharmaceutical formulations	Sonication and centrifugation	Electrochemical Sensor	20	0.56	0.97	0.97–19.42	5.9	[6]
Human plasma	Centrifugation	LC-MS/MS	13	0.0001	0.00033	0.00067–0.333	< 5.0	[7]
Electronic cigarette liquid and beverage	SPME	Extraction nanoESI-MS	< 5	0.0015 0.003	0.05 0.01	0.01–1	< 6.1	This work

*DLLME: dispersive liquid–liquid microextraction; MIP-SPE: molecular imprinted polymer-solid phase extraction; DES-LPME: deep eutectic solvent-based liquid-phase microextraction; DDSME: Drop-to-drop solvent microextraction; SPME: solid-phase microextraction, GC–NPD: gas chromatography–nitrogen phosphorus detection; ESI-IMS: electrospray ionization-ion mobility spectrometry; HPLC-UV: high-performance liquid chromatography-ultraviolet spectroscopy; UV–Vis: ultraviolet-visible spectroscopy; GC–MS: gas chromatography–mass spectrometry; LC-MS/MS: liquid chromatography-tandem mass spectrometry; nanoESI-MS: nanoelectrospray ionization-mass spectrometry.

Supplementary Figures

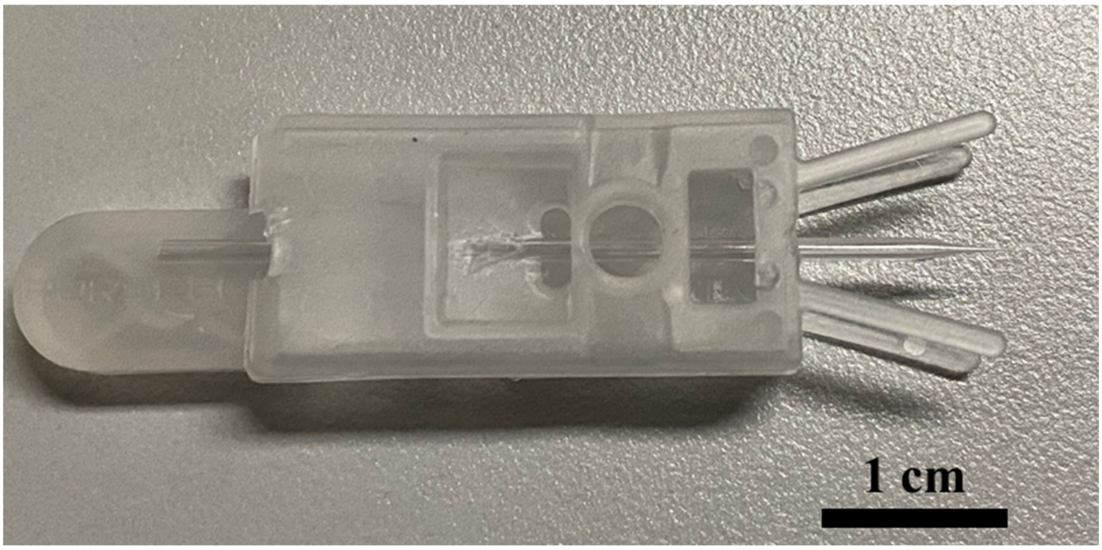

Figure S1. Photo of the custom-modified sample cartridge for miniature MS analysis.

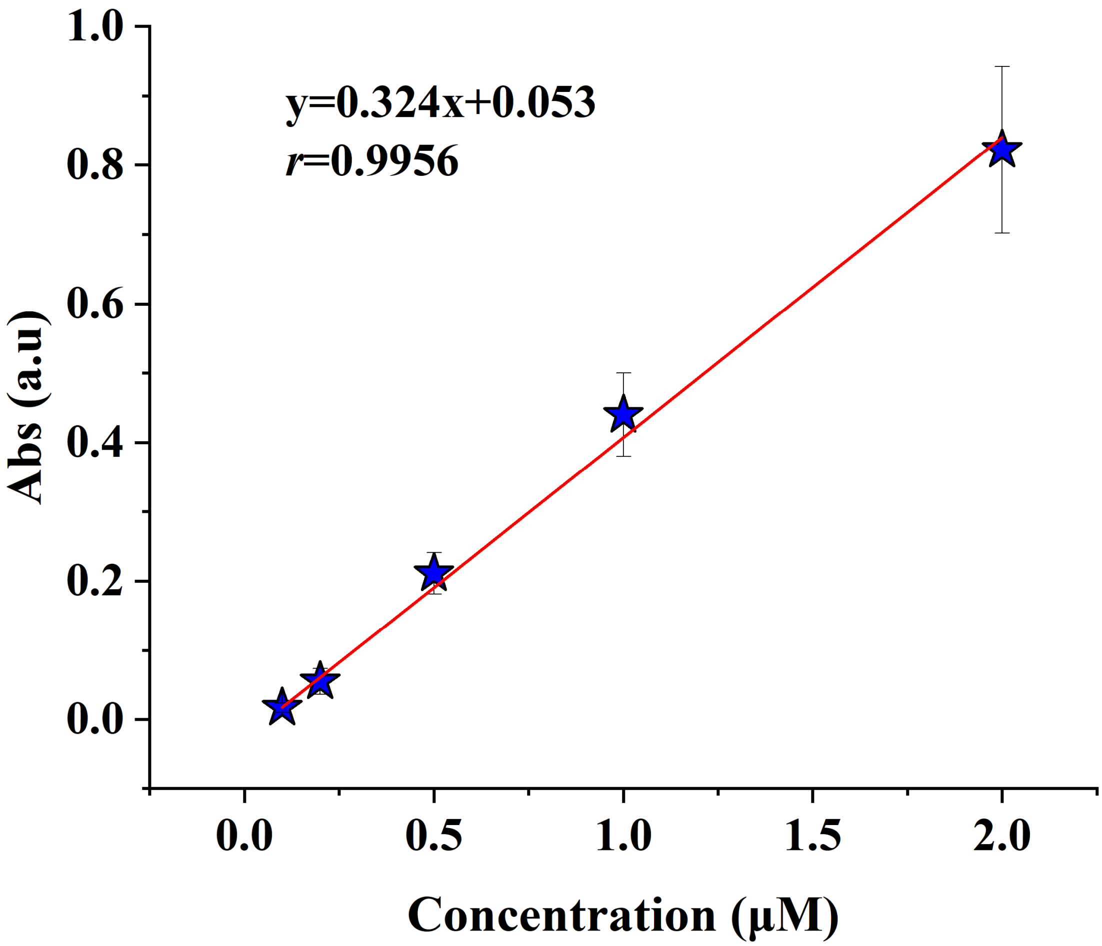

Figure S2. Calibration curve for quantitative analysis of the caffeine-specific aptamers (n = 6).

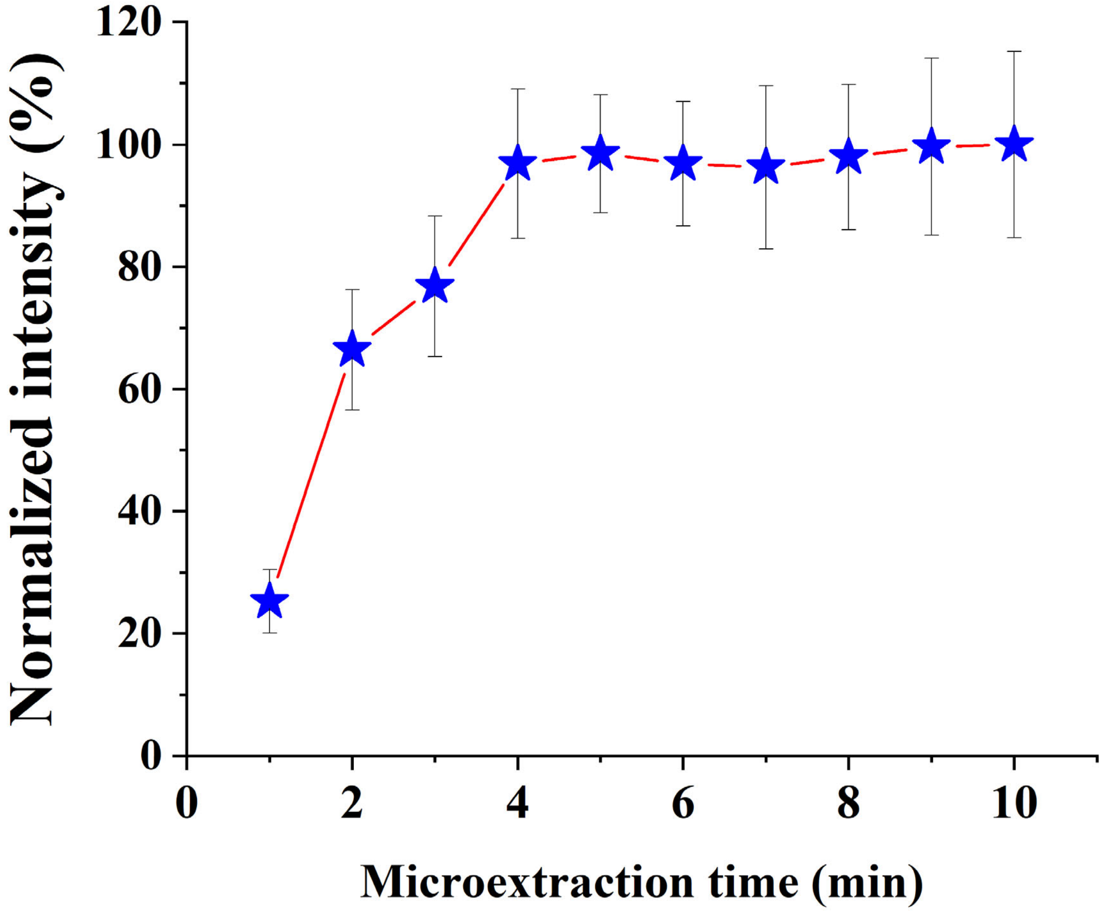

Figure S3. Optimization of microextraction time for the in-capillary aptamer-functionalized SPME process (n = 6).

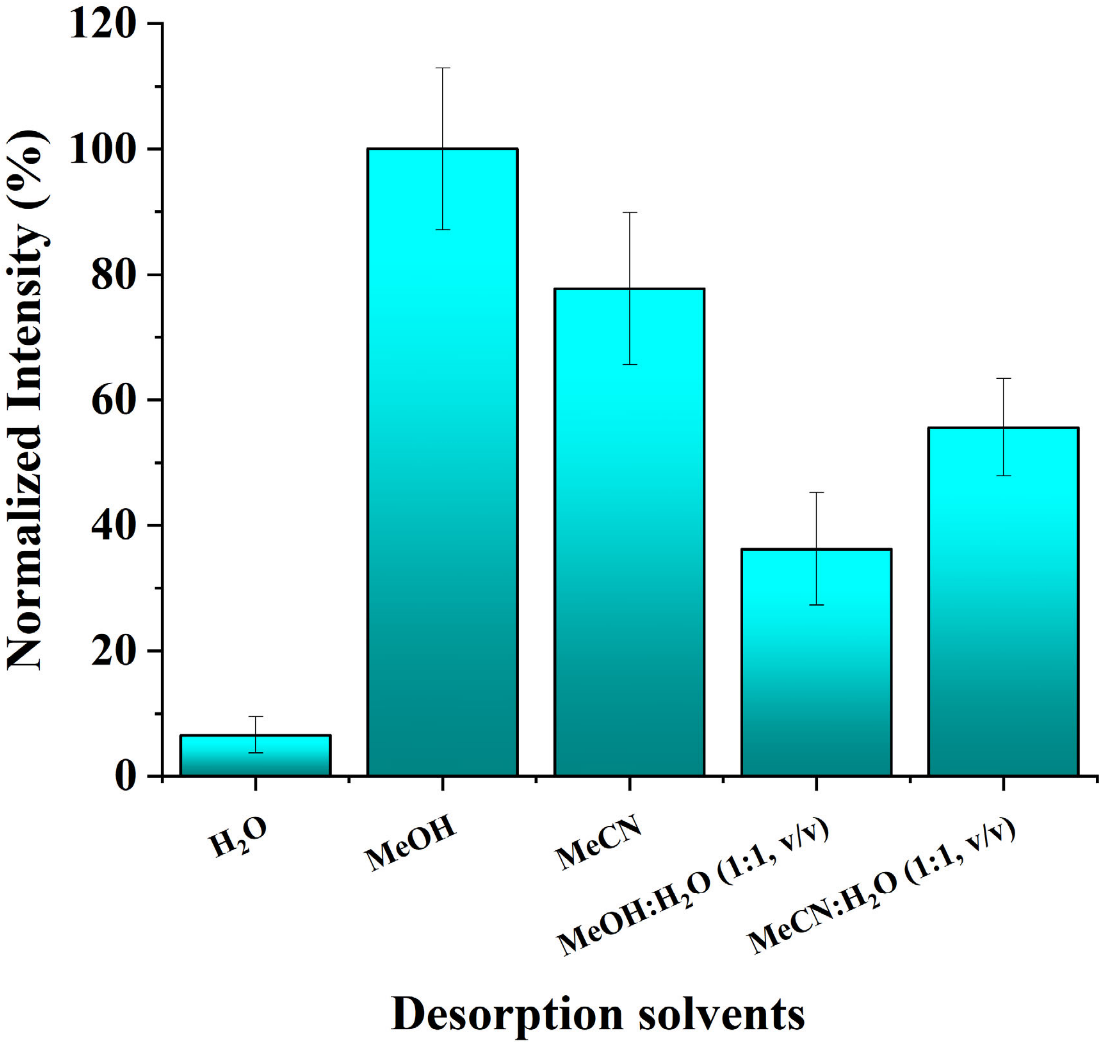

Figure S4. Optimization of desorption solvent for the in-capillary aptamer-functionalized SPME process (n = 6).

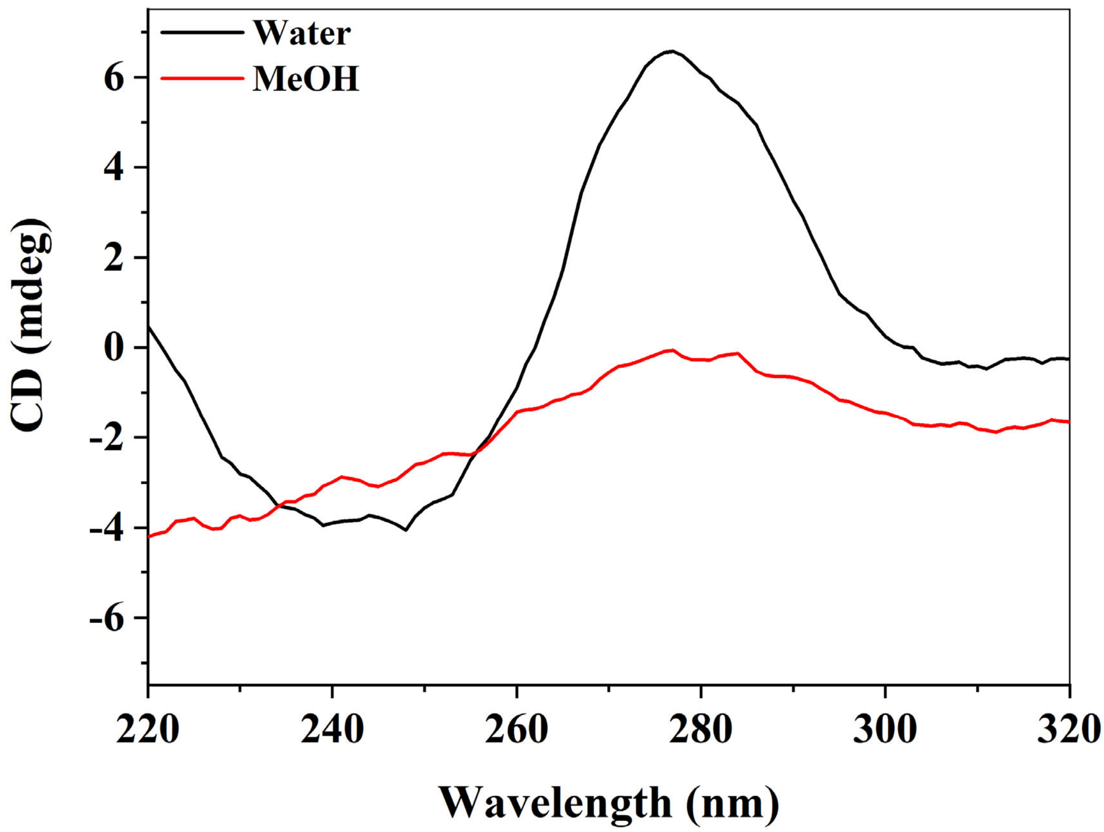

Figure S5. The CD spectra of the caffeine-specific aptamers in water and methanol.

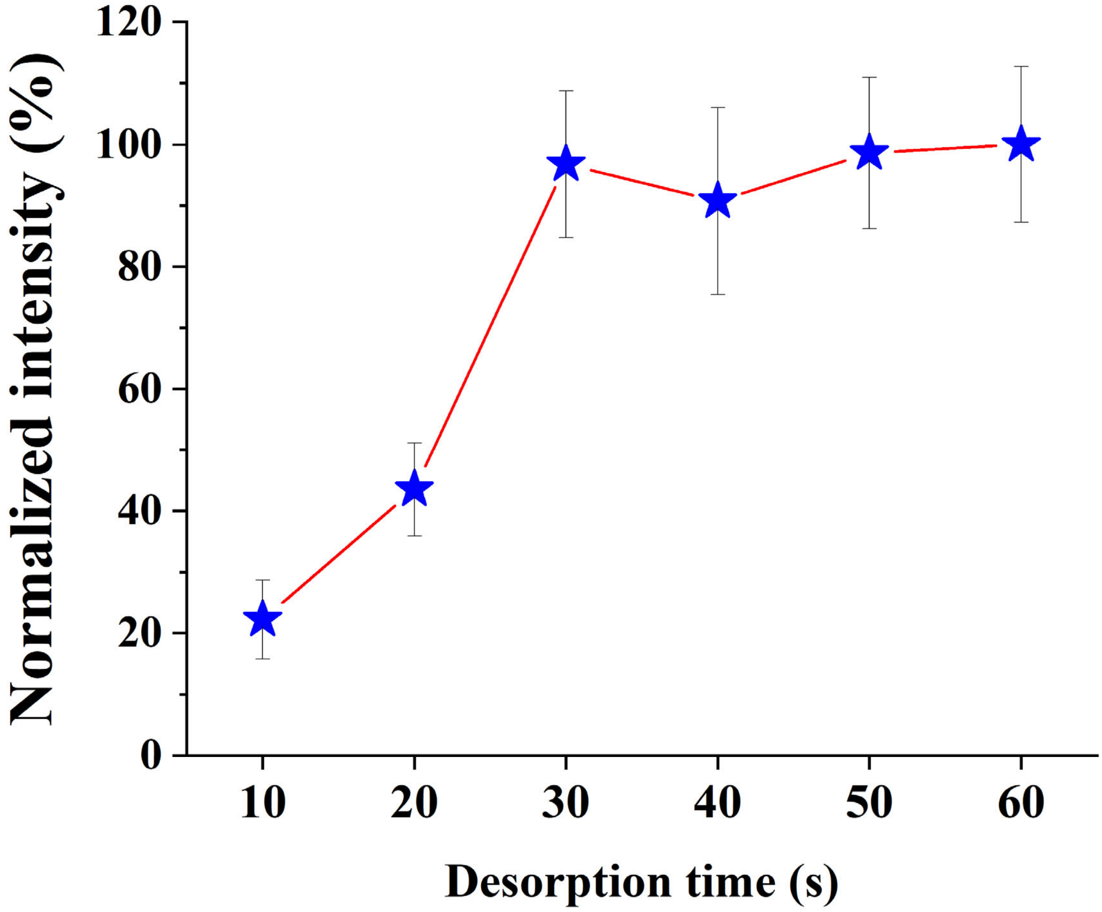

Figure S6. Optimization of desorption time for the in-capillary aptamer-functionalized SPME process (n = 6).

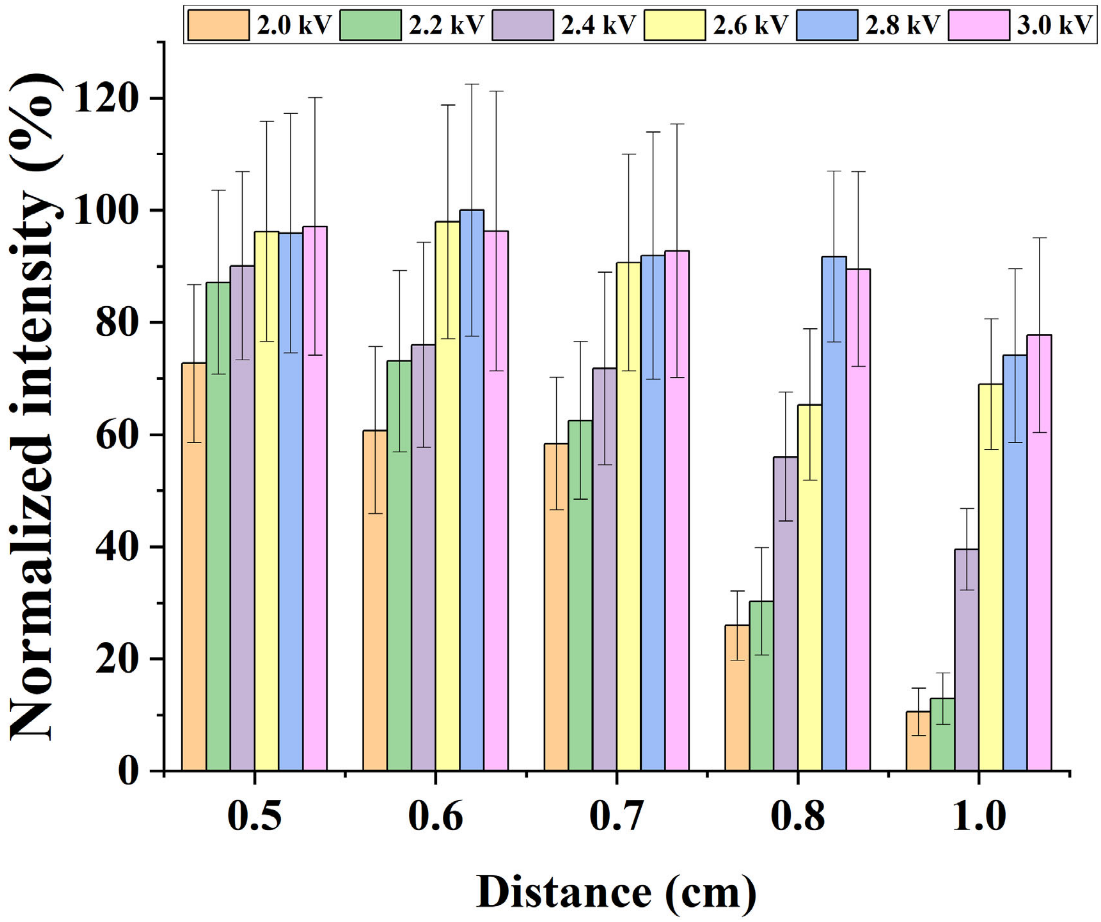

Figure S7. Optimization of capillary-to-inlet distance and electric voltage.

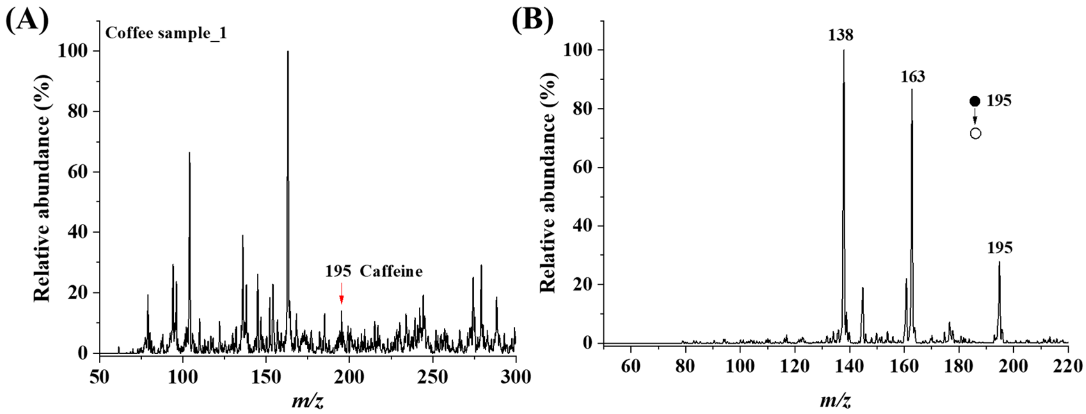

Figure S8. (A) Full-scan MS and (B) MS/MS spectra for the analysis of caffeine in a real coffee beverage sample (Americano, brand A).

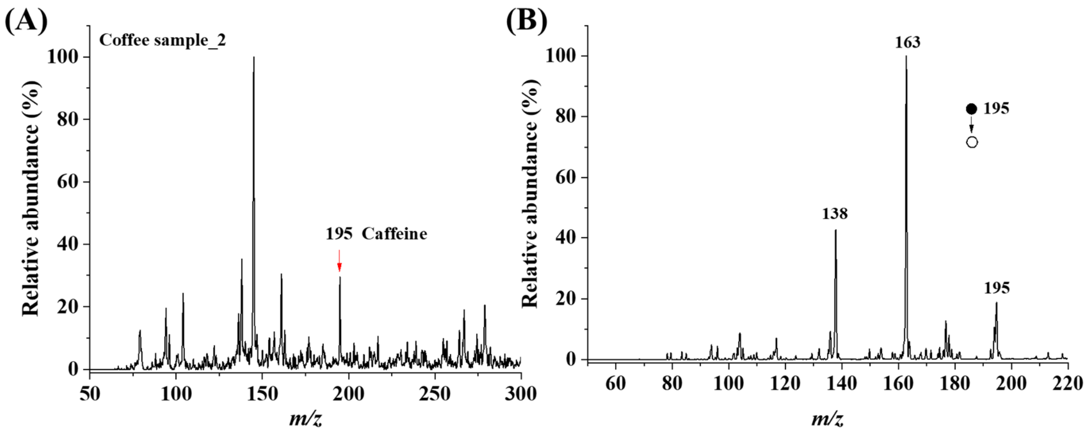

Figure S9. (A) Full-scan MS and (B) MS/MS spectra for the analysis of caffeine in a real coffee beverage sample (Americano, brand B).

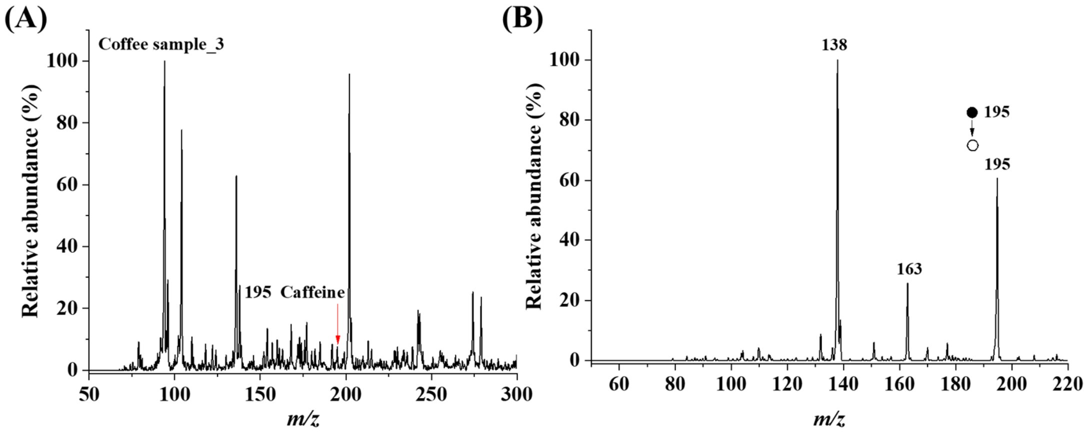

Figure S10. (A) Full-scan MS and (B) MS/MS spectra for the analysis of caffeine in a real coffee beverage sample (Americano, brand C).

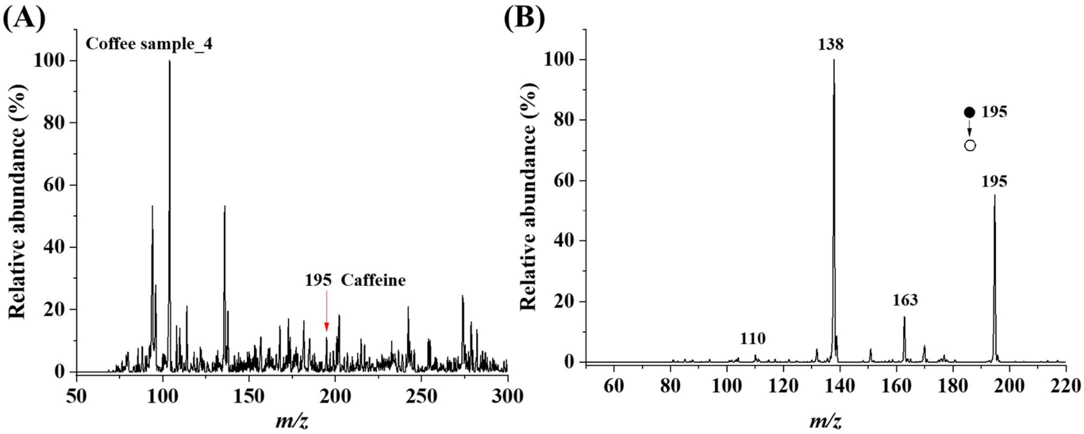

Figure S11. (A) Full-scan MS and (B) MS/MS spectra for the analysis of caffeine in a real coffee beverage sample (Mocha, brand C).

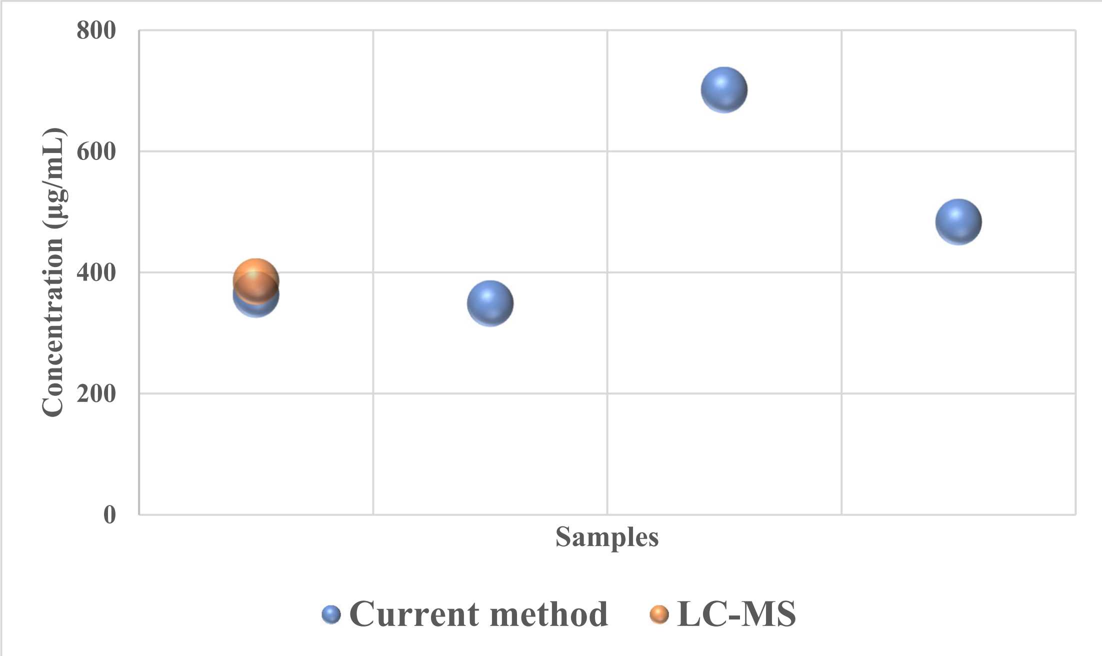

Figure S12. Quantitative analysis of caffeine in four real coffee beverage samples using the current method and a well-established LC–MS method.

References

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