

Table S1. Central composite design matrix for optimizing the pollen-grain solid-phase extraction procedure

Run	Pollen grain amount (mg)	Sample volume (mL)	Proportion of formic acid in eluting solvent (%)	Gallic acid	Protocatechuic acid	Protocatechuic acid	Vanillic acid	Caffeic acid	<i>p</i> -Coumaric acid	Ferulic acid	Sinapic acid	<i>m</i> -Coumaric acid
1	350	1.25	4.5	163995.4	380775.6	696066.2	628439.9	780872	931901	385911.2	217062.6	1364095
2	650	0.75	4.5	488987.6	684371	1226172	1243324	1563514	1733631	898931.7	648935.1	2469439
3	650	0.75	1.5	405189.7	592794.2	1079795	1041089	1440353	1465779	700007.3	483931.3	2107776
4	500	1.5	3	226421	498794.1	709544.8	635194	1077933	943583.9	390764.3	239067.2	1456049
5	500	1	3	473370	646691.3	1033719	1017045	1388980	1427334	668423.4	461210.2	2110996
6	500	1	3	435196.3	640464.9	1017420	972295.1	1365073	1357088	656292.4	448639.6	2053446
7	500	1	6	465938.5	625524.4	1028929	954856.1	1333653	1343661	593673.6	376855.3	2025476
8	500	1	3	386230.7	622713.2	1077481	1038922	1268496	1458480	665873.4	415282.7	2186873
9	500	1	3	314114.9	575354.5	896336.8	874783.3	1007201	1181371	533243.3	330581	1805732
10	500	1	3	386230.7	622713.2	1077481	1038922	1268496	1458480	665873.4	415282.7	2186873
11	650	1.25	1.5	275522.8	450813.1	1058869	1022044	1097565	1430293	677666.4	430508.9	1998943
12	800	1	3	472440.9	671864.5	1285464	1298499	1602974	1753223	893263.7	646696	2490667
13	650	1.25	4.5	297307.3	487960.8	1108618	1095087	1124465	1530855	736668.2	464511	2110550
14	500	1	3	322176.4	586771	908021.7	902650.7	1153066	1250100	578838.3	374751.5	1871139
15	500	1	0	390198.7	685466.7	1032067	1018051	1363182	1449111	690157.5	448556	2149232
16	350	0.75	1.5	371348.6	594174	974154	934730.8	1267807	1347010	631445.1	400165.5	1959485
17	350	1.25	1.5	167145.5	434967.5	841487.4	704411.3	856992.9	1088229	450006.5	249425.1	1617066
18	500	0.5	3	221459.1	569434	983324.1	953592.3	1089157	1336235	668622	414705.6	1756123
19	350	0.75	4.5	298833.5	569078.3	886591.8	812216.9	1182963	1201330	533088.7	217062.6	1364095
20	200	1	3	189077.1	313490.6	566072.8	534807.3	717865.6	741986.3	353607.5	648935.1	2469439

Table S2. Linear ranges, correlation coefficients (R^2), and sensitivities of the developed method for different phenolic acids

Analyte	Wavelength (nm)	Linearity range ($\mu\text{g mL}^{-1}$)	R^2	LOQ ($\mu\text{g mL}^{-1}$)	LOD ($\mu\text{g mL}^{-1}$)
Gallic acid	280	1.00–40.00	0.994	1.00	0.40
Protocatechuic acid	254	0.40–40.00	0.996	0.40	0.20
<i>p</i> -Hydroxybenzoic acid	254	0.40–40.00	0.996	0.40	0.20
Vanillic acid	254	0.40–40.00	0.996	0.40	0.20
Caffeic acid	310	1.00–40.00	0.993	1.00	0.40
<i>p</i> -Coumaric acid	310	0.20–20.00	0.996	0.20	0.10
Ferulic acid	310	0.20–20.00	0.997	0.20	0.10
Sinapic acid	310	0.40–40.00	0.995	0.40	0.20
<i>m</i> -Coumaric acid	280	0.20–20.00	0.998	0.20	0.10

Table S3. Intra- and inter-day precisions and relative recoveries of the developed method at three different concentration of analyte levels

Analyte	Intra-day (% RSD, n = 3)			Inter-day (% RSD, n = 9)			Relative recovery (% , n = 3)		
	Low ^a	Medium ^b	High ^c	Low ^a	Medium ^b	High ^c	Low ^a	Medium ^b	High ^c
Gallic acid	5.04	3.82	2.25	8.66	2.16	2.58	96.51	81.36	77.58
Protocatechuic acid	4.19	3.30	3.85	5.73	0.69	4.84	95.30	119.65	110.76
<i>p</i> -Hydroxybenzoic acid	4.16	0.41	4.7	11.57	1.76	7.19	97.87	114.60	99.72
Vanillic acid	2.60	2.91	4.58	11.54	2.95	4.06	91.371	107.61	87.56
Caffeic acid	4.23	2.45	4.61	8.45	1.91	5.33	89.74	112.82	84.59
<i>p</i> -Coumaric acid	3.38	1.54	4.22	11.08	3.18	8.39	102.09	117.15	100.24
Ferulic acid	6.93	1.84	3.23	10.15	4.13	7.75	103.109	110.63	100.01
Sinapic acid	6.47	1.71	2.94	9.39	4.55	6.42	83.65	103.97	83.16
<i>m</i> -Coumaric acid	7.34	2.78	3.39	10.65	8.06	5.89	111.17	118.98	107.34

^a 4 $\mu\text{g mL}^{-1}$ for gallic acid, protocatechuic acid, *p*-hydroxybenzoic acid, vanillic acid, caffeic acid, and sinapic acid; 2 $\mu\text{g mL}^{-1}$ for *p*-coumaric acid, ferulic acid, and *m*-coumaric acid.

^b 10 $\mu\text{g mL}^{-1}$ for gallic acid, protocatechuic acid, *p*-hydroxybenzoic acid, vanillic acid, caffeic acid, and sinapic acid; 5 $\mu\text{g mL}^{-1}$ for *p*-coumaric acid, ferulic acid, and *m*-coumaric acid.

^c 30 $\mu\text{g mL}^{-1}$ for gallic acid, protocatechuic acid, *p*-hydroxybenzoic acid, vanillic acid, caffeic acid, and sinapic acid; 15 $\mu\text{g mL}^{-1}$ for *p*-coumaric acid, ferulic acid, and *m*-coumaric acid.

Table S4. The optimum precursor, product ions monitored, and collision energies (CE) in MS analysis

Analyte	Precursor (m/z)	Transition (m/z)	Collision energy (V)
Gallic acid	169	125	16
		79	25
Protocatechuic	152	109	16
		91	27
<i>p</i> -Hydroxybenzoic acid	137	93.1	12
		65	32
Vanillic acid	167	152	17
		108	19
Caffeic acid	179	135	16
		107	22
<i>p</i> -Coumaric acid	163	119	16
		93	32
Ferulic acid	193	178	14
		134	15
Sinapic acid	223	193	23
		149	20
<i>m</i> -Coumaric acid	163	119	12
		93.1	8