

Supplementary Information

Determination of Volatile Organic Compounds in Andean Tomato Landraces by Headspace Solid Phase Microextraction-Gas Chromatography-Mass Spectrometry

Pablo R. Cortina,^a Ramón Asis,^b Iris E. Peralta,^{c,d} Pablo D. Asprelli^{d,e} and Ana N. Santiago^{,a}*

^a*INFIQC, Departamento de Química Orgánica and ^bCIBICI, Departamento de Bioquímica Clínica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5000 Córdoba, Argentina*

^c*IADIZA CCT CONICET Mendoza, Parque General San Martín, 5500 Mendoza, Argentina*

^d*Facultad de Ciencias Agrarias, Universidad Nacional de Cuyo y CCT CONICET Mendoza, Chacras de Coria, Luján de Cuyo, 5505 Mendoza, Argentina*

^e*EEA La Consulta, INTA, La Consulta, San Carlos, 5567 Mendoza, Argentina*

*e-mail: santiago@fcq.unc.edu.ar

Figure 1. Tomatoes picture.

a) Andean tomato landrace No 557. Mature green and ripe tomato fruit.



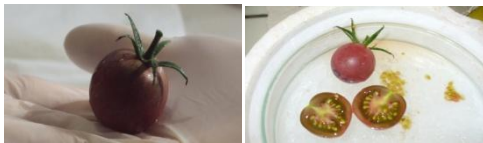
b) Andean tomato landrace No 3842. Mature green and ripe tomato fruit.



c) Andean tomato landrace No 565. Mature green and ripe tomato fruit.



d) Andean tomato landrace No 4750. Ripe tomato fruit.



e) Commercial tomato variety No 4735 (M82). Ripe tomato fruit



f) Wild tomato specie No 4739 (*Solanum pimpinellifolium*). Ripe tomato fruit.



Figure S1. Tomato images.

HS-SPME-GC-MS optimization

Table S1. Effect of different extraction fibres on tomato samples using HS-SPME-GC-MS

Compound	Grey fiber	Pink fiber	Light blue fiber	σ			CV / %		
				Grey	Pink	Light blue	Grey	Pink	Light blue
1-Penten-3-ona	5342	4126	3585	933	1957	690	17.5	47.4	19.2
<i>cis</i> -3-Hexenal	879752	1193527	978565	158863	95886	451661	18.1	8.0	46.2
<i>trans</i> -2-Hexenal	921056	445347	229785	189887	85986	95013	20.6	19.3	41.3
1-Hexanol	9735	3611	3257	4181	355	635	42.9	9.8	19.5
1-Nitropentane	13525	7857	12566	2118	1552	2288	15.7	19.8	18.2
<i>trans</i> -2-Heptenal	4173	3258	6010	418	1004	897	10.0	30.8	14.9
Benzaldehyde	44672	3211	15015	1207	6017	912	2.7	187.4	6.1
6-Methyl-5-hepten-2-one	16407	12784	10876	1509	2848	2670	9.2	22.3	24.5
Camphor	17962	18644	16987	3260	4683	4577	18.1	25.1	26.9
2-Undecanone	56850	70273	89105	3256	5150	8491	5.7	7.3	9.5
Geranyl acetone	18529	5828	5294	1177	4379	1288	6.4	75.1	24.3
β -Ionone	2955	1788	915	608	1015	1496	20.6	56.8	163.5
Average CV / %							15.6	42.4	34.5

σ : Standard deviation with n = 3. Marked in green are highlighted the highest area values obtained for each compound.

Fibre optimization - total area

	Grey fiber	Pink fiber	Light blue fiber	σ		
				Grey	Pink	Light blue
Total selected VOCs area	1990958	1770254	1371960	367417	210832	570618
Total CV / %				18.5	11.9	41.6

Table S2. Effect of different extraction times on tomato samples using HS-SPME-GC-MS

Compound	30 min	40 min	50 min	σ			CV / %		
				30 min	40 min	50 min	30 min	40 min	50 min
3-Methylbutanal	13407	12475	12022	2209	2589	2471	16.5	20.8	20.6
Pentanal	8317	13212	8776	121	967	2814	1.5	7.3	32.1
1-Penten-3-ona	21422	18027	10268	1631	2356	2896	7.6	13.1	28.2
3-Methyl-1-butanol	10217	7512	5812	459	1382	2764	4.5	18.4	47.6
<i>cis</i> -3-Hexenal	1810000	1521000	530787	131093	190930	51093	7.2	12.6	9.6
Heptanal	11443	18645	14450	109	4501	8855	1.0	24.1	61.3
Benzaldehyde	27308	39733	22410	15222	2749	575	55.7	6.9	2.6
6-Methyl-5-hepten-2-one	34677	72514	53263	11863	1133	12762	34.2	1.6	24.0
Octanal	18101	19981	13447	2003	2175	5878	11.1	10.9	43.7
<i>cis</i> -Linalyl oxide	22180	111504	29325	9064	31649	12046	40.9	28.4	41.1
Camphor	78082	211183	185495	22569	20245	4661	28.9	9.6	2.5
2-Undecanone	96737	267924	182554	3435	18822	136630	3.6	7.0	74.8
β -Damascenone	319002	492768	539308	71939	8405	158603	22.6	1.7	29.4
Average CV / %							18.1	12.5	32.1

σ : standard deviation with n = 3. Marked in green are highlighted the highest area values obtained for each compound.

Extraction time - total area

	30 min	40 min	50 min	σ		
				30 min	40 min	50 min
Total selected VOCs area	2470893	2806478	1607917	271717	287903	402048
Total CV / %				11.0	10.3	25.0

Table S3. Effect of different extraction temperatures on tomato samples using HS-SPME-GC-MS

Compound	40 °C	50 °C	60 °C	σ			CV / %		
				40 °C	50 °C	60 °C	30 min	40 min	50 min
2-Metilfuran	21881	17779	4439	1083	4298	2370	4.9	24.2	53.4
1-Penten-3-ona	34498	28574	5397	12806	4648	3968	37.1	16.3	73.5
3-Methyl-1-butanol	40731	28230	25180	814	3744	8713	2.0	13.3	34.6
<i>cis</i> -3-Hexenal	2202000	1660900	1551600	373339	253442	422885	17.0	15.3	27.3
<i>trans</i> -2-Hexenal	1590000	1263680	1684000	932553	298489	134458	58.7	23.6	8.0
6-Methyl-5-hepten-2-one	57350	65582	71806	10221	7387	19161	17.8	11.3	26.7
2-Isobutylthiazole	21892	28095	19813	936	4125	9420	4.3	14.7	47.5
2-Ethyl-1-hexanol	1272000	884245	754965	182434	103187	77195	14.3	11.7	10.2
Phenylacetaldehyde	28123	79447	72433	2381	1749	12822	8.5	2.2	17.7
<i>cis</i> -Linalyl oxide	82478	143575	163607	3270	15446	87208	4.0	10.8	53.3
α -Terpineol	392982	408720	430612	17080	3181	48344	4.3	0.8	11.2
Methyl salicylate	127715	335102	545254	5479	43459	188766	4.3	13.0	34.6
β -Damascenone	81974	229170	552274	60439	186650	65351	73.7	81.4	11.8
Geranyl acetone	22159	36338	40807	1184	17080	2913	5.3	47.0	7.1
Average CV / %							18.3	20.4	29.8

σ : standard deviation with n = 3. Marked in green are highlighted the highest area values obtained for each compound.

Extraction temperature - total area

	40 °C	50 °C	60 °C	σ		
				40 °C	50 °C	60 °C
Total selected VOCs area	5975783	5209437	5922187	1604019	946885	1083574
Total CV / %				26.8	18.2	18.3

Table S4. Effect of inorganic salt addition on tomato samples using HS-SPME-GC-MS

Compound	Without salt	CaCl ₂	NaCl	σ			CV / %		
				Without salt	CaCl ₂	NaCl	Without salt	CaCl ₂	NaCl
3-Methylbutanal	199535	806993	994425	96741	93827	33508	48.5	11.6	3.4
1-Penten-3-ona	90736	78834	82090	19054	9705	11350	21.0	12.3	13.8
3-Methyl-1-butanol	749999	1484933	75324	189510	364607	6340	25.3	24.6	8.4
<i>cis</i> -3-Hexenal	1.79E+05	3.34E+06	2.72E+05	1.64E+05	1.08E+06	2.03E+05	91.6	32.3	74.6
<i>trans</i> -2-Hexenal	135064	818307	2298024	98561	177160	374694	73.0	21.6	16.3
<i>trans</i> -2-Heptenal	476988	1355719	878277	53271	708529	263674	11.2	52.3	30.0
6-Methyl-5-hepten-2-one	152185	165182	196017	9751	13407	34220	6.4	8.1	17.5
2-Isobutylthiazole	9126	44513	79675	1407	25764	9185	15.4	57.9	11.5
<i>cis</i> -Linalyl oxide	991014	1637591	713636	418947	137975	87597	42.3	8.4	12.3
Linalool	422936	968921	299532	26415	110518	58418	6.2	11.4	19.5
2-Phenylethanol	12666	217774	79252	10801	17298	16442	85.3	7.9	20.7
Benzyl nitrile	27715	40515	65804	5586	5180	4403	20.2	12.8	6.7
Methyl salicylate	513325	1202507	516238	98504	138316	162531	19.2	11.5	31.5
<i>p</i> -Menth-1-en-9-al	305474	670010	242970	61284	91634	32811	20.1	13.7	13.5
β-Ionone	12069	289175	119608	3651	5837	18330	30.3	2.0	15.3
Average CV / %							34.4	19.2	19.7

σ: standard deviation with n = 3. Marked in green are highlighted the highest area values obtained for each compound.

Inorganic salt - total area

	Without salt	CaCl ₂	NaCl	σ		
				Without salt	CaCl ₂	NaCl
Total selected VOCs area	4277832	13120974	6912872	1257483	2979757	1316503
Total CV / %				29.4	22.7	19.0

Table S5. Effect of added CaCl₂ amount on tomato samples using HS-SPME-GC-MS

Compound	CaCl ₂								CV / %			
					σ							
	0.75 g	1.5 g	2.2 g	3 g	0.75 g	1.5 g	2.2 g	3 g	0.75 g	1.5 g	2.2 g	3 g
3-Methyl-butanal	384408	457670	587817	617358	18173	84004	23143	134775	4.7	18.4	3.9	21.8
1-Penten-3-one	97810	134043	144303	47908	8809	18741	11740	9705	9.0	14.0	8.1	20.3
2-Ethylfuran	19163	48265	45241	28898	2287	27941	19740	9035	11.9	57.9	43.6	31.3
3-Methyl-1-butanol	27398	62463	75137	20656	4468	8461	13387	5037	16.3	13.5	17.8	24.4
<i>cis</i> -3-Hexenal	4588217	4460004	4314342	5477767	1408217	2460004	1314320	1477675	30.7	55.2	30.5	27.0
Hexanal	5017127	4674501	3218756	6142835	507127	667450	981875	1142835	10.1	14.3	30.5	18.6
<i>trans</i> -2-Hexenal	6286942	5361745	5501033	7369341	1628942	1167451	350103	1693417	25.9	21.8	6.4	23.0
1-Hexanol	162567	84929	75311	0	66782	39451	29441	0	41.1	46.5	39.1	
<i>trans</i> -2-Heptenal	406986	1346831	1063384	406436	21279	36701	321855	112835	5.2	2.7	30.3	27.8
6-Methyl-5-hepten-2-one	157330	247290	373728	0	46840	70081	101572	0	29.8	28.3	27.2	
2-Isobutylthiazole	79954	61513	54513	11750	47510	39722	12006	2141	59.4	64.6	22.0	18.2
Phenylacetaldehyde	83972	91359	114076	95620	9233	13947	16848	25641	11.0	15.3	14.8	26.8
<i>cis</i> -Linalyl oxide	392355	999390	1402892	1821155	72975	132954	384995	200152	18.6	13.3	27.4	11.0
Camphor	225823	123796	209818	343366	92173	14604	23320	134675	40.8	11.8	11.1	39.2
α -Terpineol	272682	517095	335461	134975	57279	66701	128755	11435	21.0	12.9	38.4	8.5
<i>p</i> -Menth-1-en-9-al	195148	674912	636093	216963	19428	86516	105108	76417	10.0	12.8	16.5	35.2
Geranyl acetone	22156	47346	29657	11840	1642	4651	8503	7341	7.4	9.8	28.7	62.0
Average CV / %									20.8	24.3	23.3	26.3

σ : standard deviation with n = 3. Marked in green are highlighted the highest area values obtained for each compound.

CaCl₂ amount - total area

					σ			
	0.75 g	1.5 g	2.2 g	3 g	0.75 g	1.5 g	2.2 g	3 g
Total selected VOCs area	18420038	19393152	18181562	22746868	4013164	4939380	3846711	5043116
Total CV / %					21.8	25.5	21.2	22.2

Table S6. Effect of EDTA solution addition on tomato samples using HS-SPME-GC-MS

Compound	σ								CV / %			
	CaCl ₂		CaCl ₂ -EDTA/NaOH		CaCl ₂		CaCl ₂ -EDTA/NaOH		CaCl ₂		CaCl ₂ -EDTA/NaOH	
	1.5 g	2.2 g	1.5 g	2.2 g	1.5 g	2.2 g	1.5 g	2.2 g	1.5 g	2.2 g	1.5 g	2.2 g
2-Metilfuran	17251	15531	10751	<u>29712</u>	3612	4534	729	638	20.9	29.2	6.8	2.1
1-Penten-3-ona	139203	158705	97526	<u>129240</u>	18741	11740	8180	9961	13.5	7.4	8.4	7.7
3-Methyl-1-butanol	68991	71938	57409	<u>81064</u>	9276	14774	2733	5739	13.4	20.5	4.8	7.1
<i>cis</i> -3-Hexenal	5123774	4692072	6670194	<u>7407521</u>	2219741	1523644	1309137	696085	43.3	32.5	19.6	9.4
<i>trans</i> -2-Hexenal	4974520	5478414	4085706	<u>4781914</u>	1351201	832189	770416	597953	27.2	15.2	18.9	12.5
1-Nitropentane	113969	49682	70045	<u>95637</u>	43827	3950	6095	16970	38.5	8.0	8.7	17.7
<i>trans</i> -2-Heptenal	1283700	937242	816285	<u>1189062</u>	40284	296044	97249	81240	3.1	31.6	11.9	6.8
Octanal	11842	15375	28241	<u>36119</u>	3571	1742	2704	3184	30.2	11.3	9.6	8.8
2-Isobutylthiazole	68309	45627	<u>119728</u>	80410	36271	12877	11543	13687	53.1	28.2	9.6	17.0
2-Phenylethanol	217774	146648	113054	<u>182413</u>	46860	22601	18371	10761	21.5	15.4	16.2	5.9
Benzyl nitrile	61327	80605	48732	<u>73108</u>	9237	6785	5136	8490	15.1	8.4	10.5	11.6
Methyl salicylate	1382514	1001542	1279514	<u>1670521</u>	241762	126738	97381	266604	17.5	12.7	7.6	16.0
2,4-Decadienal	34007	49203	27960	<u>36795</u>	7038	8812	4612	5106	20.7	17.9	16.5	13.9
Geranyl acetone	51048	31702	30994	<u>47923</u>	4651	8503	2790	5228	9.1	26.8	9.0	10.9
Average CV%									23.4	18.9	11.3	10.5

σ : standard deviation with n = 3; Marked in green are highlighted the highest area values obtained for each compound. The maximum values of the two best conditions with and without EDTA solution are underlined for each compound.

EDTA solution - total area

	σ							
	CaCl ₂		CaCl ₂ -EDTA		CaCl ₂		CaCl ₂ -EDTA	
	1.5 g	2.2 g	1.5 g	2.2 g	1.5 g	2.2 g	1.5 g	2.2 g
Total selected VOCs Area	13548229	12774286	13456139	15841439	4036072	2874933	2337076	1721646
Total CV / %					29.8	22.5	17.4	10.9

Table S7. Volatile compounds identified in tomato samples

VOCs code	Average normalized area						VOCs code	Standard deviation					
	4735	4739	4750	3842	565	557		4735	4739	4750	3842	565	557
M1	0.7048	0.9024	0.2039	0.1612	0.2253	0.2667	M1	0.0630	0.4383	0.0526	0.1398	0.1779	0.1881
M2	1.4825	83.8196	2.2933	1.9779	1.8719	1.3376	M2	0.2380	9.1198	1.1118	1.1087	1.6624	1.1006
M3	0.2164	0.2313	0.1945	0.1387	0.5986	0.2054	M3	0.0912	0.3572	0.0465	0.0288	0.5262	0.1141
M4	45.1796	117.9327	82.8342	15.9136	89.7944	102.1149	M4	4.0195	13.8259	13.7353	0.6079	5.6111	57.2514
M5	1.8356	10.5404	4.2623	0.7328	5.0504	2.1774	M5	0.4264	4.5173	1.3267	0.2280	1.6174	1.1474
M6	0.5828	0.5984	0.4499	0.3548	0.1781	0.5305	M6	0.0777	0.2065	0.0521	0.0877	0.1544	0.2521
M7	1.4017	8.7247	7.8730	1.7529	1.2622	0.8492	M7	0.6437	1.6457	3.9965	1.6258	0.6143	0.3006
M8	4.2915	4.0138	1.8259	0.6242	3.7248	1.7838	M8	2.1938	2.0120	0.6607	0.2502	2.3648	0.1237
M9	0.7116	1.0965	0.2976	0.0000	0.5219	0.4005	M9	0.4556	1.0386	0.1183	0.0000	0.1297	0.3241
M10	18.3744	49.9600	35.2996	3.5972	18.8864	40.3510	M10	4.3751	10.7629	10.2330	0.2572	1.2090	23.7752
M11	8.4080	11.7227	9.6878	10.7797	5.7670	20.7785	M11	3.1810	2.7848	0.5975	3.3394	1.0396	8.7847
M12	609.8605	1157.4821	696.2767	211.7964	777.9981	572.9642	M12	102.5245	389.7329	98.7857	27.8747	65.5719	275.4311
M13	340.0601	409.3404	334.4983	149.8699	414.8530	198.4561	M13	112.6789	31.3136	31.6114	46.8557	180.9641	73.0435
M14	32.3673	79.3789	50.7471	9.7849	28.7724	37.7589	M14	7.0962	11.4101	7.1190	2.7294	11.4350	27.2553
M15	447.5736	1786.6955	1077.4564	188.3528	871.8656	757.0939	M15	86.0262	241.3962	87.9543	49.2732	128.0376	513.6521
M16	1.7786	3.0898	1.7379	1.1683	0.2305	1.3319	M16	0.1870	0.3348	0.1338	0.1985	0.0978	0.4003
M17	0.8046	1.1940	0.5625	0.3795	7.1913	0.8667	M17	0.1230	0.1767	0.1602	0.3315	3.1305	0.5285
M18	0.0283	0.0612	0.2402	0.1648	0.1104	0.3654	M18	0.0362	0.0546	0.3644	0.0901	0.0336	0.2706
M19	0.0000	0.1168	0.0000	0.0000	0.0000	0.0040	M19	0.0000	0.0833	0.0000	0.0000	0.0000	0.0047
M20	0.5852	1.0265	0.4089	0.1498	0.0000	0.2879	M20	0.1014	0.2669	0.1105	0.0454	0.0000	0.0643
M21	14.1658	3.8459	1.5388	3.2980	5.4975	2.7908	M21	4.3626	0.7691	0.8358	2.0456	3.4760	2.3790
M22	0.2619	0.2121	0.0836	0.1053	0.1590	0.3594	M22	0.0236	0.1433	0.1448	0.0126	0.0004	0.1720
M23	0.8677	6.0065	0.1664	0.4577	1.1181	5.3106	M23	0.2440	2.2339	0.1807	0.2200	0.7762	4.3794
M24	28.9634	40.4885	20.8674	7.2490	6.6808	7.9203	M24	1.7704	4.9395	3.7508	2.1338	3.4908	2.0603
M25	0.7591	0.9712	3.4796	1.1399	2.2834	6.4888	M25	0.1323	0.5004	0.9122	0.8262	0.5278	3.8422

VOCs code	Average normalized area						VOCs code	Standard deviation					
	4735	4739	4750	3842	565	557		4735	4739	4750	3842	565	557
M26	20.9407	44.1656	14.2682	21.1346	39.5414	37.7720	M26	1.3717	1.1948	3.5128	5.4199	6.0080	14.0842
M27	47.7326	145.6438	64.3545	18.9290	58.3070	42.3108	M27	14.3734	57.0512	17.7292	4.5760	4.2166	29.7641
M28	177.4308	167.2121	58.9184	101.2340	138.4493	84.0792	M28	27.4513	11.9254	8.4041	45.3532	80.6982	47.4363
M29	45.1744	71.1649	20.8637	19.5622	89.5909	39.4794	M29	6.5402	34.7973	13.2488	6.8567	38.2757	10.9119
M30	0.0000	0.0000	0.2102	0.0000	0.0501	0.1079	M30	0.0000	0.0000	0.3464	0.0000	0.0608	0.1772
M31	19.0903	32.0258	12.9616	9.5847	12.6320	14.8615	M31	2.3326	12.5541	8.5331	0.2708	2.0499	6.2600
M32	5.7842	5.7569	4.3171	6.9263	7.7907	6.6430	M32	0.7083	0.7564	1.2183	1.0307	1.4708	4.4464
M33	0.0000	0.6084	2.3031	29.5184	2.6915	4.6401	M33	0.0000	0.1282	2.3395	1.4816	0.4813	1.3772
M34	3.5228	1.0138	2.4232	0.9365	1.2393	1.9694	M34	0.8358	0.4111	0.7087	0.3474	0.1987	0.8671
M35	1.5183	237.9109	4.5473	2.1699	3.8386	5.7962	M35	0.3313	65.6375	3.1451	0.5699	1.5729	4.1890
M36	30.0049	38.5459	28.8553	46.5633	41.9726	34.8697	M36	4.8380	8.6477	1.9155	3.0308	6.9363	15.4851
M37	67.9821	101.2861	57.5622	18.1028	99.5848	61.5799	M37	15.4097	45.1608	11.1817	5.3359	70.2954	46.3327
M38	4.2595	8.9629	5.1673	4.2623	9.4434	8.9881	M38	0.8922	1.7496	2.0428	2.0206	4.4883	3.7118
M39	45.7757	370.2853	6.5532	22.5928	9.9901	41.9666	M39	8.6323	35.8577	1.2576	12.6127	1.1189	20.2381
M40	9.0025	63.3817	45.9714	3.9601	7.6359	18.0380	M40	1.5065	5.4691	11.4294	3.0527	1.9566	7.3362
M41	1.6733	2.4514	3.3951	3.9193	11.9815	17.0340	M41	0.2210	1.3617	3.4005	3.1899	3.7304	10.1103
M42	2.9738	23.7999	12.8315	1.0870	2.2730	5.6035	M42	0.6474	3.6709	3.4966	0.8985	0.5501	2.3096
M43	28.1186	33.6430	27.3230	27.7395	30.7593	26.6625	M43	0.9554	4.2560	5.1071	3.4724	5.0950	8.5546
M44	39.0728	65.3320	2.2310	3.9192	6.7389	3.6413	M44	19.8392	32.6766	1.3607	4.1126	0.3348	2.2458
M45	0.8317	0.0000	0.0000	29.3549	21.2802	39.0477	M45	0.5417	0.0000	0.0000	6.8352	6.3971	32.4932
M46	10.7455	13.2967	31.3194	18.4698	53.4777	73.4332	M46	1.8110	2.2142	21.9156	11.2631	18.2207	33.4077
M47	57.4866	82.6657	8.7101	26.8936	36.9570	17.2315	M47	7.4817	20.3803	2.5638	4.9675	11.2669	9.7389
M48	2.0192	30.4936	2.8128	2.8014	2.6919	2.0515	M48	1.8358	7.8001	1.9621	1.1175	0.5313	1.9197
M49	11.3635	11.7410	12.2411	4.9117	5.1443	11.5169	M49	1.8312	1.3397	1.9506	0.5504	1.2643	2.9888
M50	89.1642	458.9723	5.5459	120.8156	99.9048	82.4200	M50	6.8880	40.4609	4.2177	31.6651	9.5230	42.3947
M51	2.3797	2.6086	2.4973	3.0929	4.2130	2.7435	M51	0.1278	0.0553	0.0965	0.4461	0.8879	0.8919
M52	20.0348	24.3253	14.6870	47.6357	63.0914	23.2931	M52	0.7455	8.8262	7.4015	1.9881	11.1247	9.9665

VOCs code	Average normalized area						VOCs code	Standard deviation					
	4735	4739	4750	3842	565	557		4735	4739	4750	3842	565	557
M53	27.9414	65.7723	24.7303	0.0000	111.6150	1.9999	M53	41.3190	60.3741	41.8279	0.0000	193.3228	1.0634
M54	14.2242	54.9892	0.1579	4.3521	14.5675	6.3777	M54	9.0301	4.1377	0.0331	3.1314	2.2636	2.9676
M55	114.6009	122.9781	106.3093	172.4572	196.9868	116.4739	M55	10.8768	24.7553	31.2255	8.1130	33.0015	22.3104
M56	13.8184	28.0265	55.9579	92.3259	149.9131	17.3098	M56	3.1334	4.1266	27.4798	69.6372	67.4478	8.2950
M57	3.2398	14.6772	13.4732	3.4326	4.4183	6.7144	M57	0.4708	0.8613	3.2333	3.4630	1.7319	3.6250
M58	16.1761	13.6721	23.3438	16.0335	32.1070	53.9951	M58	2.4994	1.3976	2.4299	18.0265	14.7219	39.2049
M59	2.7302	6.5274	2.0560	14.6159	17.8750	0.0000	M59	0.9631	1.6552	1.7152	3.7674	6.3843	0.0000
M60	0.0000	1.8870	17.3185	478.8588	702.8350	476.3612	M60	0.0000	0.7598	12.0337	213.4682	302.4534	287.2726
M61	6.8717	10.9026	4.0549	9.6321	10.4838	4.7323	M61	0.2077	0.5434	1.4219	1.3202	2.7712	1.0612
M62	59.4501	280.8065	155.5580	100.3166	155.2621	159.3438	M62	3.9516	62.5818	74.0656	72.1038	77.2901	79.3049
M63	169.9322	36.7707	102.3875	518.1960	308.7082	104.8746	M63	72.0033	8.1695	23.0399	399.8524	351.0393	125.5138
M64	9.6555	12.6119	5.3912	24.1099	44.1848	11.1062	M64	0.6031	5.5384	4.1675	4.6193	14.7292	4.7008
M65	11.1298	8.4615	4.5899	10.2812	243.8860	7.5233	M65	0.1999	1.1570	1.1001	4.3436	98.1615	2.0090
M66	1.0221	4.0195	2.3440	0.0000	0.0000	1.0174	M66	0.2183	0.1739	2.2222	0.0000	0.0000	0.2174
M67	8.0627	7.2099	5.9670	11.7316	13.6799	7.4186	M67	1.5287	1.3409	1.3798	0.4213	2.0162	1.1509
M68	2.7707	4.5330	1.0154	0.0000	4.5026	0.0000	M68	1.4306	1.7219	0.8075	0.0000	2.0898	0.0000
M69	85.7876	47.7807	22.1327	99.9552	182.0953	50.5189	M69	8.6270	11.6938	5.4296	42.8224	80.3795	19.9808
M70	156.2954	174.1888	96.3248	227.3412	340.2276	191.5356	M70	13.8697	63.8136	71.6324	19.9618	64.1735	53.8722
M71	4.9531	8.8876	4.3122	79.8616	214.4110	44.8701	M71	0.8709	3.3906	1.5777	37.1611	107.1086	29.9719
M72	3.6243	3.9141	2.6751	3.8648	4.5079	4.3304	M72	0.0488	0.7141	1.7443	0.0956	0.7473	1.0619
M73	5.8319	3.4689	3.6106	24.7117	27.4115	7.2970	M73	0.8512	0.8502	0.7237	2.7380	6.9692	1.5946
M74	0.8888	0.9425	0.4294	0.1576	0.2356	0.9320	M74	0.2009	0.5470	0.4055	0.1785	0.2326	0.5489
M75	0.6771	0.5964	0.2271	0.6921	1.4084	0.6121	M75	0.0958	0.3730	0.3468	0.1315	0.7873	0.4791
M76	11.1580	23.2936	24.7956	8.8310	13.8906	10.5482	M76	9.3713	25.1211	21.4015	9.5646	7.8928	8.8259
M77	0.0000	0.0000	0.0000	42.0842	24.2524	3.4407	M77	0.0000	0.0000	0.0000	17.6211	22.0319	3.7739
M78	1.7134	0.9008	1.0306	1.9769	1.9164	1.6889	M78	0.4274	0.1784	0.4276	0.1177	0.4156	1.2401
M79	0.2723	0.6527	3.0497	2.4453	31.4445	0.0000	M79	0.0748	0.6669	4.7533	0.7467	17.4940	0.0000

VOCs code	Average normalized area						VOCs code	Standard deviation					
	4735	4739	4750	3842	565	557		4735	4739	4750	3842	565	557
M80	50.8116	14.8874	31.4842	136.6949	331.8888	106.1040	M80	13.5545	3.7103	9.5683	39.7364	63.9420	80.7109
M81	18.0491	7.1860	10.1032	24.7505	44.7328	13.1219	M81	1.5838	0.7353	8.8105	4.6624	12.8468	5.7913
M82	17.6491	15.5813	3.4335	19.5661	158.3594	8.4189	M82	9.6791	9.6043	1.6575	8.7139	127.1488	1.3781
M83	12.0140	8.1996	8.0555	15.8516	20.2454	11.5222	M83	2.6086	1.1819	2.7386	0.7082	4.4390	2.8584
M84	2.8277	1.2043	1.4097	4.7350	12.7121	3.7349	M84	0.5545	0.5280	0.5331	2.2010	1.7245	2.2451
M85	155.5633	92.2541	6.5019	284.9299	572.8730	62.2388	M85	14.4603	34.9244	3.9108	117.6977	334.9168	53.7276
M86	3.0861	1.7917	1.3054	8.9079	9.3434	3.7977	M86	0.7867	0.3638	1.2355	3.7430	2.5847	3.0898
M87	0.5281	1.9444	1.4699	0.9926	4.2341	2.9059	M87	0.2312	1.5298	1.0483	0.7660	2.3935	3.3634
M88	6.5653	10.3863	11.0131	4.4593	8.1086	3.9958	M88	8.3484	11.8014	9.7862	7.1161	1.0898	4.3726
M89	14.5812	17.3550	4.0310	33.4322	47.9839	9.5409	M89	4.4562	4.3473	1.7335	15.4478	9.8042	8.5673
M90	1.7705	3.1759	0.5313	41.8006	9.7502	0.8980	M90	0.7665	0.9013	0.2279	34.4125	5.0441	0.2721
M91	0.9907	1.8570	0.5508	2.3796	0.9572	0.8909	M91	0.2081	0.3583	0.4326	0.7563	0.4784	0.8041
M92	4.2084	16.8457	12.1281	0.0000	6.9153	4.9415	M92	2.0927	1.3383	2.7966	0.0000	3.1385	3.7688
M93	3.1403	2.7989	1.8537	27.4320	19.1709	5.1862	M93	0.5476	0.5363	1.3463	25.7516	5.5503	4.8190
M94	3.5171	2.1991	2.4929	24.3794	31.2452	8.3714	M94	1.0299	0.7376	1.2385	0.7840	3.1827	7.6688
M95	3.8655	2.4901	2.5945	14.1871	16.5320	7.2267	M95	0.8881	0.6315	0.8879	1.7394	2.6032	6.3835
M96	4.4720	5.0603	3.8939	51.1182	60.6779	15.5447	M96	0.7923	1.5048	1.4841	1.1988	8.7650	15.6711
M97	1.4554	0.1602	0.2984	5.7014	0.0000	1.2326	M97	0.1447	0.1435	0.2621	1.8915	0.0000	1.3222
M98	0.3614	0.2692	0.2528	1.8649	2.0807	0.3050	M98	0.1680	0.1708	0.1787	0.9488	0.6334	0.1601
M99	3.9109	1.9411	1.6873	19.4115	19.9911	5.3643	M99	0.8240	0.2418	0.6417	3.9690	2.2374	3.8872
M100	2.9171	3.1842	1.5675	7.6966	10.7075	4.6613	M100	0.6377	0.2857	1.4709	0.6561	2.5913	4.9244
M101	0.4977	0.3867	0.1918	2.1165	1.9888	1.4514	M101	0.1679	0.0520	0.0423	0.1903	0.5760	1.9126

Table S8. Novel VOCs identified in tomato samples

No.	VOCs code	Name	IUPAC Name	CAS Number	Category
1	M9	<i>cis,cis</i> -1,4-pentadiene	<i>cis,cis</i> -1,4-pentadiene	591-93-5	hydrocarbon
2	M10	<i>trans</i> -4-pentenal	<i>trans</i> -4-pentenal	2100-17-6	aldehyde
3	M25	geranic oxide	2,6,6-trimethyl-2-vinyltetrahydropyran	7392-19-0	heterocycle
4	M44	2-methyl-3-phenyl-1-propene	2-methyl-3-phenyl-1-propene	3290-53-7	hydrocarbon
5	M48	2-methylacetophenone	2-methylacetophenone	577-16-2	ketone
6	M52	3-methylheptyl acetate	3-methylheptyl acetate	72218-58-7	ester
7	M57	DMHEX	3,6-dimethyl-2,3,3a,4,5,7a-hexahydrobenzofuran	70786-44-6	heterocycle
8	M73	duraldehyde	2,4,5-trimethylbenzaldehyde	5779-72-6	aldehyde
9	M75	(3 <i>E</i>)-4-methyl-3-hepten-3-one	(3 <i>E</i>)-4-methyl-3-hepten-3-one	22319-25-1	ketone
10	M78	TRIMCICL	(1 <i>E</i>)-2-propanone-1-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)	16695-72-0	ketone
11	M81	2-methyl-2-octen-4-one	2-methyl-2-octen-4-one	19860-71-0	ketone
12	M83	verdyl acetate	3a,4,5,6,7,7a-hexahydro-4,7-methano-1 <i>H</i> -inden-6-ol acetate	5413-60-5	ester
13	M87	lilial	3-(4- <i>tert</i> -butylphenyl)-2-methylpropanal	80-54-6	aldehyde
14	M92	1-phenyl-1-propanol	1-phenyl-1-propanol	93-54-9	alcohol
15	M93	ar-himachalen-2-ol	3,5,5,9-tetramethyl-6,7,8,9-tetrahydrobenzo[7]annulen-2-ol	119660-66-1	alcohol
16	M94	propyl salicylate	2-hydroxy-benzoic acid propylester	607-90-9	ester
17	M96	isoamyl salicylate	2-hydroxybenzoic acid-3-methylbutylester	87-20-7	ester
18	M98	β -methyl ionone	1-(2,6,6-trimethyl-1-cyclohexen-1-yl)-1-penten-3-one	127-43-5	ketone
19	M99	benzophenone	benzophenone	119-61-9	ketone
20	M100	8-pentadecanone	8-pentadecanone	818-23-5	ketone
21	M101	α -hexyl cinnamaldehyde	(2 <i>E</i>)-2-benzylideneoctanal	101-86-0	aldehyde

Table S9. Analysis of variance (ANOVA) of novel VOCs in tomato samples

VOCs code	4739	4735	4750	557	565	3842
M9	1.1 ± 1.0 ^a	0.7 ± 0.5 ^a	0.3 ± 0.1 ^a	0.4 ± 0.3 ^a	0.5 ± 0.1 ^a	0.0 ± 0.0 ^a
M10	50.0 ± 10.8 ^b	18.4 ± 4.4 ^a	35.3 ± 10.2 ^b	40.4 ± 23.8 ^b	18.9 ± 1.2 ^a	3.6 ± 0.3 ^b
M25	1.0 ± 0.5 ^a	0.8 ± 0.1 ^a	3.5 ± 0.9 ^a	6.5 ± 3.8 ^b	2.3 ± 0.5 ^a	1.1 ± 0.8 ^a
M44	65.3 ± 32.7 ^b	39.1 ± 19.8 ^b	2.2 ± 1.4 ^a	3.6 ± 2.3 ^a	6.7 ± 0.3 ^a	3.9 ± 4.1 ^a
M48	30.5 ± 7.8 ^b	2.0 ± 1.8 ^a	2.8 ± 2.0 ^a	2.1 ± 1.9 ^a	2.7 ± 0.5 ^a	2.8 ± 1.1 ^a
M52	24.3 ± 8.8 ^a	20.0 ± 0.8 ^a	14.7 ± 7.4 ^a	23.3 ± 10.0 ^a	63.1 ± 11.1 ^c	47.6 ± 2.0 ^b
M57	14.7 ± 0.9 ^b	3.2 ± 0.5 ^a	13.5 ± 3.2 ^b	6.7 ± 3.6 ^a	4.4 ± 1.7 ^a	3.4 ± 3.5 ^a
M73	3.5 ± 0.9 ^a	5.8 ± 0.9 ^a	3.6 ± 0.7 ^a	7.3 ± 1.6 ^a	27.4 ± 7.0 ^b	24.7 ± 2.7 ^b
M75	0.6 ± 0.4 ^a	0.7 ± 0.1 ^a	0.2 ± 0.4 ^a	0.6 ± 0.5 ^a	1.4 ± 0.8 ^b	0.7 ± 0.1 ^a
M78	0.9 ± 0.2 ^a	1.7 ± 0.4 ^a	1.0 ± 0.4 ^a	1.7 ± 1.2 ^a	1.9 ± 0.4 ^a	2.0 ± 0.1 ^a
M81	7.2 ± 0.7 ^a	18.1 ± 1.6 ^a	10.1 ± 8.8 ^a	13.1 ± 5.8 ^a	44.7 ± 12.9 ^b	24.8 ± 4.7 ^a
M83	8.2 ± 1.2 ^a	12.0 ± 2.6 ^a	8.1 ± 2.7 ^a	11.5 ± 2.9 ^a	20.3 ± 4.4 ^b	15.9 ± 0.7 ^b
M87	1.9 ± 1.5 ^a	0.5 ± 0.2 ^a	1.5 ± 1.1 ^a	2.9 ± 3.4 ^a	4.2 ± 2.4 ^a	1.0 ± 0.8 ^a
M92	16.9 ± 1.3 ^c	4.2 ± 2.1 ^b	12.1 ± 2.8 ^c	4.9 ± 3.8 ^b	6.9 ± 3.1 ^b	0.0 ± 0.0 ^a
M93	2.8 ± 0.5 ^a	3.1 ± 0.6 ^a	1.9 ± 1.4 ^a	5.2 ± 4.8 ^a	19.2 ± 5.6 ^a	27.4 ± 25.8 ^a
M94	2.2 ± 0.7 ^a	3.5 ± 1.0 ^a	2.5 ± 1.2 ^a	8.4 ± 7.7 ^a	31.3 ± 3.2 ^c	24.4 ± 0.8 ^b
M96	5.1 ± 1.5 ^a	4.5 ± 0.8 ^a	3.9 ± 1.5 ^a	15.5 ± 15.7 ^a	60.7 ± 8.8 ^b	51.1 ± 1.2 ^b
M98	0.3 ± 0.2 ^a	0.4 ± 0.2 ^a	0.3 ± 0.2 ^a	0.3 ± 0.2 ^a	2.1 ± 0.6 ^b	1.9 ± 1.0 ^b
M99	1.9 ± 0.2 ^a	3.9 ± 0.8 ^a	1.7 ± 0.6 ^a	5.4 ± 3.9 ^a	20.0 ± 2.2 ^b	19.4 ± 4.0 ^b
M100	3.2 ± 0.3 ^a	2.9 ± 0.6 ^a	1.6 ± 1.5 ^a	4.7 ± 4.9 ^a	10.7 ± 2.6 ^b	7.7 ± 0.7 ^b
M101	0.4 ± 0.1 ^a	0.5 ± 0.2 ^a	0.2 ± 0.0 ^a	1.5 ± 1.9 ^b	2.0 ± 0.6 ^b	2.1 ± 0.2 ^b

Different letters in the same row indicate significant differences ($p < 0.05$).

Table S10. Classification and cross validation results by discriminant analysis of VOCs in tomato samples

Accession	557	565	3842	4735	4739	4750	Total	Error / %
557	3	0	0	0	0	0	3	0
565	0	3	0	0	0	0	3	0
3842	0	0	3	0	0	0	3	0
4735	0	0	0	3	0	0	3	0
4739	0	0	0	0	3	0	3	0
4750	0	0	0	0	0	3	3	0
Total	3	3	3	3	3	3	18	0