Supporting Information

Cryogenic Free Comprehensive Multidimensional Gas Chromatography Using a Deans Switch for Improved Analysis of Petrochemical Products Derived from Palmitic Acid Oxidation

Nilobon Thongdorn-Ae[1], Thumnoon Nhujak[2], Pannipa Janta[2], Atitarn Rueangthaweep[1], Napida Hinchiranan[3,4,5*] and Chadin Kulsing[2,*]

[1] Program in Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand.

[2]Chromatographic Separation and Flavor Chemistry Research Unit and Center of Molecular Sensory Science, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand.

[3]Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

[4]Center of Excellence on Petrochemical and Materials Technology (PETROMAT), Chulalongkorn University, Bangkok 10330, Thailand

[5]Center of Excellence in Catalysis for Bioenergy and Renewable Chemicals (CBRC), Chulalongkorn University, Bangkok 10330, Thailand

Analytical Methods

*Authors for Correspondence:

Napida Hinchiranan

Tel: +6622187518

Email: napida.h@chula.ac.th

Chadin Kulsing

Tel: +66802971178

Email: chadin.k@chula.ac.th

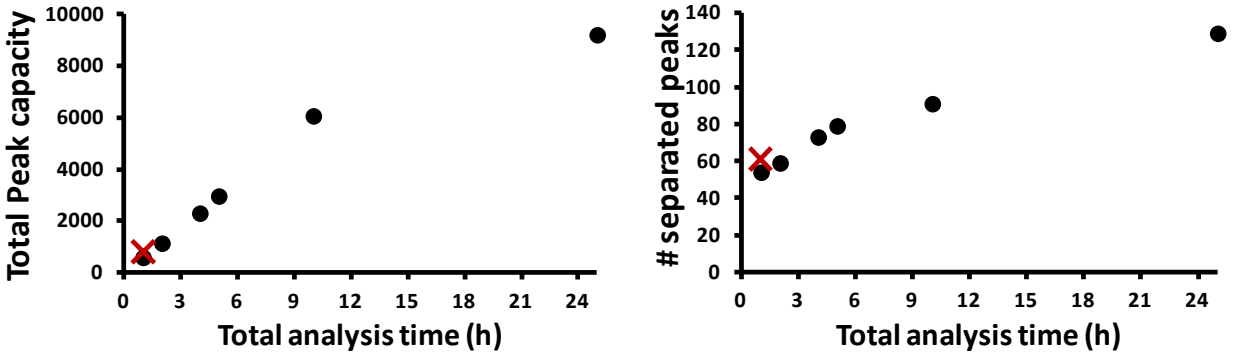

Figure S1. Plots of total peak capacity (left) and number of separated peaks (right) vs total CH/C analysis time obtained from the CH/C analysis of a petrochemical sample (●), compared with the data point obtained from GC×GC analysis using a flow modulator (✕) for the same sample.

Table S1. The H/C events for each injection (run) of the comprehensive H/C analysis with the H/C window of 0.2 min.

Run	Heart-cut range (min)					
1	3.0-3.2	8.0-8.2	13.0-13.2	18.0-18.2	23.0-23.2	28.0-28.2
2	3.2-3.4	8.2-8.4	13.2-13.4	18.2-18.4	23.2-23.4	28.2-28.4
3	3.4-3.6	8.4-8.6	13.4-13.6	18.4-18.6	23.4-23.6	28.4-28.6
4	3.6-3.8	8.6-8.8	13.6-13.8	18.6-18.8	23.6-23.8	28.6-28.8
5	3.8-4.0	8.8-9.0	13.8-14.0	18.8-19.0	23.8-24.0	28.8-29.0
6	4.0-4.2	9.0-9.2	14.0-14.2	19.0-19.2	24.0-24.2	29.0-29.2
7	4.2-4.4	9.2-9.4	14.2-14.4	19.2-19.4	24.2-24.4	29.2-29.4
8	4.4-4.6	9.4-9.6	14.4-14.6	19.4-19.6	24.4-24.6	29.4-29.6
9	4.6-4.8	9.6-9.8	14.6-14.8	19.6-19.8	24.6-24.8	29.6-29.8
10	4.8-5.0	9.8-10.0	14.8-15.0	19.8-20.0	24.8-25.0	29.8-30.0
11	5.0-5.2	10.0-10.2	15.0-15.2	20.0-20.2	25.0-25.2	30.0-30.2
12	5.2-5.4	10.2-10.4	15.2-15.4	20.2-20.4	25.2-25.4	30.2-30.4
13	5.4-5.6	10.4-10.6	15.4-15.6	20.4-20.6	25.4-25.6	30.4-30.6
14	5.6-5.8	10.6-10.8	15.6-15.8	20.6-20.8	25.6-25.8	30.6-30.8
15	5.8-6.0	10.8-11.0	15.8-16.0	20.8-21.0	25.8-26.0	30.8-31.0
16	6.0-6.2	11.0-11.2	16.0-16.2	21.0-21.2	26.0-26.2	31.0-31.2
17	6.2-6.4	11.2-11.4	16.2-16.4	21.2-21.4	26.2-26.4	31.2-31.4
18	6.4-6.6	11.4-11.6	16.4-16.6	21.4-21.6	26.4-26.6	31.4-31.6
19	6.6-6.8	11.6-11.8	16.6-16.8	21.6-21.8	26.6-26.8	31.6-31.8
20	6.8-7.0	11.8-12.0	16.8-17.0	21.8-22.0	26.8-27.0	31.8-32.0
21	7.0-7.2	12.0-12.2	17.0-17.2	22.0-22.2	27.0-27.2	32.0-32.2
22	7.2-7.4	12.2-12.4	17.2-17.4	22.2-22.4	27.2-27.4	32.2-32.4
23	7.4-7.6	12.4-12.6	17.4-17.6	22.4-22.6	27.4-27.6	32.4-32.6
24	7.6-7.8	12.6-12.8	17.6-17.8	22.6-22.8	27.6-27.8	32.6-32.8
25	7.8-8.0	12.8-13.0	17.8-18.0	22.8-23.0	27.8-28.0	32.8-33.0

Table S2. Volatile compound profile of the ODH product in water obtained using the Rancimat method analyzed by using SPME 1DGC−MS.

No.	Name	t_R (min)	Retention index			Match score		Area ($\times 10^7$)
			Experiment	Literature	Difference	Match	R Match	
1	2-Pentanone	2.61	680	685	5	753	878	0.596
2	3-Penten-2-one	3.25	733	734	1	840	856	0.072
3	Toluene	3.68	761	763	2	914	928	0.645
4	2-Hexanone	4.05	785	790	5	875	899	1.725
5	4-Methyl-3-penten-2-one	4.25	798	798	0	685	703	0.169
6	3-Hexen-2-one	5.14	835	845	10	712	744	0.320
7	(R)-(+)-3-Methylcyclopentanone	5.29	841	848	7	827	876	0.168
8	(E)-2-Hexenal	5.48	849	854	5	680	816	0.004
9	5-Methyl-2-hexanone	5.58	853	862	9	659	759	0.004
10	Ethylbenzene	5.67	857	855	-2	798	950	0.003
11	5-Hepten-2-one	6.04	872	866	-6	819	853	0.318
12	3-Heptanone	6.33	884	887	3	755	756	0.220
13	2-Heptanone	6.44	888	891	3	878	878	1.364
14	Cyclohexanone	6.47	889	894	5	715	749	0.339
15	2-Methyl-2-hexenal	6.54	892	884	-8	655	679	0.113
16	Heptanal	6.74	900	901	1	764	799	0.043
17	2-Methyl-2-cyclopenten-1-one	6.88	905	913	8	793	836	0.049
18	1-Cyclopentyl-ethanone	7.59	927	941	14	784	806	0.274
19	Cyclooctane	7.84	935	927	-8	700	752	0.178
20	2-Methyl-cyclohexanone	8.11	943	953	10	820	822	0.147
21	3-Methyl-cyclohexanone	8.19	945	958	13	881	896	0.094
22	3-Ethylcyclopentanone	8.41	952	962	10	795	820	0.145
23	Benzaldehyde	8.53	956	962	6	928	934	1.714
24	4-Octanone	8.98	970	976	6	797	851	0.144
25	Benzonitrile	9.32	981	985	4	715	921	0.855
26	2-Octanone	9.58	989	990	1	862	874	1.260
27	6-Octen-2-one	9.80	996	985	-11	707	825	0.093
28	Cycloheptanone	10.20	1007	1015	8	910	919	0.303
29	3,4,5-Trimethyl-2-cyclopenten-1-one	10.74	1022	1033	11	690	832	0.032
30	3-Octen-2-one	10.97	1029	1040	11	665	666	0.234
31	(E)-2-Octenal	11.92	1056	1060	4	660	689	0.065
32	Acetophenone	12.15	1062	1065	3	902	931	0.186
33	1-Octanol	12.37	1068	1071	3	675	729	0.026
34	8-Nonen-2-one	12.80	1080	1085	5	812	856	0.174

35	3-Nonanone	12.92	1084	1090	6	793	845	0.056
36	3-(Hydroxymethyl)-2-Nonanone	13.10	1089	1093	4	909	968	0.297
37	Cyclooctanone	13.93	1112	1115	3	682	809	0.027
38	Methyl ester octanoic acid	14.29	1122	1126	4	751	795	0.002
39	2-Propyl-cyclohexanone	14.52	1129	1135	6	669	697	0.027
40	Naphthalene	16.25	1177	1182	5	772	850	0.024
41	2-Decanone	16.67	1189	1193	4	811	833	0.041
42	Methyl ester 8-nonenoic acid	17.51	1213	1216	3	708	791	0.004
43	2-Undecanone	20.15	1289	1294	5	666	769	0.004

t_R = retention time

Table S3. Volatile compound profile of the ODH product in water obtained using the Rancimat method analyzed by using SPME CH/C 2DGC–FID/MS. The average difference between experimental and literature retention indices was within ±16.

No.	Name	Retention time (min)			Retention index (*I*)			Match score		Area* (x10^7)
		^1t_R+^2t_R	^1t_R	^2t_R	Exper-iment	Litera-ture	Differ-ence	Matc h	R match	
1	Tetrahydrofuran	7.84	4.5	3.3	632	623	9	691	848	0.695
2	2-Butanone	8.03	4.5	3.5	632	598	34	855	908	1.636
3	2-Butenal	9.79	4.5	5.3	632	629	3	780	843	0.713
4	(E)-2-Butenal	9.83	4.7	5.1	649	647	2	823	839	2.532
5	1-Butanol	11.31	4.7	6.6	649	659	10	828	856	1.836
6	2-Pentanone	9.34	5.1	4.2	683	685	2	826	826	45.700
7	3-Pentanol	10.86	5.1	5.8	683	690	7	655	869	0.186
8	3-Methyl-2-butanol	11.04	5.1	5.9	683	674	9	792	835	0.652
9	2-Butenenitrile	11.95	5.1	6.9	683	664	19	673	842	0.334
10	Pentanal	9.40	5.3	4.1	700	699	1	717	723	15.800
11	2-Pentanol	11.08	5.3	5.8	700	703	3	750	835	0.484
12	3-Penten-2-one	11.77	5.7	6.1	724	734	9	874	881	4.647
13	3-Methyl-1-butanol	12.88	5.7	7.2	724	736	12	805	858	1.125
14	Methyl Isobutyl Ketone	10.16	5.9	4.3	736	735	1	670	891	0.359
15	2-Methyl-2-butenal	11.39	5.9	5.5	736	746	10	754	866	0.526
16	(E)-3-Penten-2-one	11.80	5.9	5.9	736	735	1	882	882	18.500
17	3-Methyl-2-pentanone	10.47	6.1	4.4	748	752	4	790	907	1.570
18	(E)-2-Pentenal	12.01	6.1	5.9	748	754	6	846	850	1.695
19	Pyridine	12.99	6.1	6.9	748	746	2	734	842	0.483
20	1-Pentanol	13.89	6.3	7.6	760	765	5	903	912	14.100
21	Toluene	11.04	6.5	4.5	772	763	9	912	912	21.800
22	3,5-Hexadien-2-ol	12.14	6.5	5.6	772	781	9	783	783	22.900
23	Pentanenitrile	13.28	6.5	6.9	772	738	34	896	905	8.944

24	3-Hexanone	11.24	6.7	4.5	784	784	0	884	922	38.000
25	2-Hexanone	11.65	6.7	5.0	784	790	6	823	826	107.000
26	2-Methyl-1-penten-3-one	11.79	6.7	5.1	784	748	36	705	795	0.244
27	4-Methyl-3-penten-2-one	12.55	6.9	5.7	796	798	2	927	935	14.200
28	3-Hexanol	13.11	6.9	6.2	796	797	1	835	873	1.247
29	Cyclopentanone	13.49	6.9	6.6	796	791	5	937	873	25.400
30	Tetrahydro-2-methyl-2H-pyran	10.81	7.1	3.7	806	838	32	693	771	0.473
31	Hexanal	11.84	7.1	4.7	806	800	6	725	728	26.200
32	3-Hexen-2-one(RI=811)	12.59	7.1	5.5	806	811	5	829	834	8.660
33	2-Hexanol	13.58	7.1	6.5	806	801	5	731	766	3.754
34	Hexamethyl-cyclotrisiloxane	10.16	7.5	2.7	822	851	29	896	900	2.976
35	2-Methyl-2-pentenal	13.15	7.5	5.7	822	837	15	655	780	0.286
36	4-Hexen-3-one	13.88	7.7	6.2	830	855	25	882	882	6.598
37	3-Ethyl-2-pentanone	12.57	7.9	4.7	839	838	1	667	854	0.397
38	2-Methyl-cyclopentanone	14.15	7.9	6.3	839	846	7	923	935	24.600
39	3-Hexen-2-one(RI=845)	14.27	7.9	6.4	839	845	6	903	913	20.900
40	2-Cyclopenten-1-one	17.05	7.9	9.2	839	831	8	814	846	1.208
41	3-Methyl-2-hexanone	12.84	8.1	4.7	847	844	3	824	859	0.752
42	4-Methyl-2-hexanone	13.00	8.1	4.9	847	848	1	725	845	0.255
43	3-Methyl-cyclopentanone	14.58	8.1	6.5	847	853	6	862	880	7.388
44	5-Methyl-2-hexanone	13.38	8.3	5.1	855	862	7	711	853	0.827
45	(E)-2-Hexenal	14.53	8.3	6.2	855	854	1	733	848	1.189
46	Tetrahydro-2-furanmethanol	12.81	8.5	4.3	863	885	22	717	820	0.673
47	1,3-Dimethyl-benzene	13.48	8.5	5.0	863	866	3	733	851	0.611
48	1-Hexanol	16.55	8.5	8.1	863	868	5	854	886	5.547
49	Tetrahydro-2-(methoxymethyl)-Furan	12.83	8.7	4.1	871	859	12	757	797	1.755
50	4-Heptanone	13.47	8.7	4.8	871	872	1	888	888	15.400
51	5-Hepten-2-one	14.81	8.7	6.1	871	866	5	773	821	59.800
52	Hexanenitrile	16.07	8.9	7.2	880	877	3	893	920	10.100
53	(E,E)-2,4-Hexadienal	17.19	8.9	8.3	880	911	31	701	763	0.568
54	3-Heptanone	14.02	9.1	4.9	888	887	1	862	863	53.200
55	1-Methyl-cyclohexanol	14.44	9.1	5.3	888	908	20	751	754	153.000
56	Cyclohexanol	17.91	9.1	8.8	888	881	7	760	842	0.506
57	2-Heptanone	14.48	9.3	5.2	896	891	5	828	831	62.900
58	2-Methyl-2-hexenal	15.33	9.3	6.0	896	884	12	708	713	54.600
59	5-Methyl-3-hexen-2-one	15.58	9.3	6.3	896	875	21	747	748	22.800
60	3-Heptanol	15.78	9.3	6.5	896	877	19	845	853	4.204

61	2-Heptanol	16.20	9.3	6.9	896	900	4	864	875	3.820
62	Cyclohexanone	16.56	9.3	7.3	896	894	2	862	863	73.700
63	4-Cyclopentene-1,3-dione	17.26	9.3	8.0	896	881	15	711	802	2.136
64	2-Propyltetrahydropyran	13.37	9.5	3.9	904	911	7	773	829	0.814
65	Heptanal	14.64	9.5	5.1	904	901	3	874	874	20.500
66	2-Methyl-2-cyclopenten-1-one	17.86	9.7	8.2	911	913	2	915	917	18.500
67	Deltacyclene	13.47	9.9	3.6	918	924	6	811	816	81.900
68	5,5-Dimethyl-2(5H)-furanone	16.00	9.9	6.1	918	952	34	735	756	3.550
69	Anisole	17.33	9.9	7.4	918	920	2	782	900	0.329
70	4-Oxohex-2-enal	16.30	10.3	6.0	933	957	24	808	825	4.644
71	1-Cyclopentyl-ethanone	16.56	10.3	6.3	933	941	8	785	846	75.400
72	3-Hepten-2-one	16.80	10.3	6.5	933	937	4	856	857	12.300
73	2-Cyclohexen-1-one	19.46	10.3	9.2	933	920	13	881	883	5.685
74	4-Methyl-2-heptanone	15.54	10.5	5.0	940	943	3	799	846	0.831
75	Cyclohexanecarboxaldehyde	16.75	10.5	6.3	940	963	23	727	787	0.388
76	3,5-Dimethyl-cyclohexene	17.64	10.5	7.1	940	912	28	771	773	28.300
77	2-propenyl-Benzene	15.02	10.7	4.3	947	934	13	856	858	43.900
78	3-Methyl-2-heptanone	15.64	10.7	4.9	947	937	10	875	885	2.301
79	2-Methyl-cyclohexanone	17.44	10.7	6.7	947	953	6	902	916	53.200
80	3-Methyl-cyclohexanone	17.81	10.7	7.1	947	958	11	873	894	2.202
81	α-Methylstyrene	15.02	10.9	4.1	955	976	21	906	918	47.000
82	6-Methyl-2-heptanone	16.17	10.9	5.3	955	956	1	763	811	2.264
83	4-Methyl-cyclohexanone	17.85	10.9	7.0	955	959	4	853	872	74.400
84	5-Methyl-2-heptanone	16.57	11.1	5.5	962	971	9	857	912	2.059
85	2-Methyl-, 2-methyl-2-propenyl ester propanoic acid	16.69	11.1	5.6	962	927	35	670	753	4.124
86	(E)-2-Heptenal	17.52	11.1	6.4	962	958	4	805	873	3.935
87	3-Ethylcyclopentanone	17.88	11.1	6.8	962	962	0	907	910	20.000
88	2-Butyltetrahydro-furan	15.85	11.3	4.6	969	1004	35	694	861	6.595
89	1-Cyclohexyl-ethanone	17.27	11.3	6.0	969	985	16	735	797	43.200
90	2-Methyl-1-hepten-6-one	17.44	11.3	6.1	969	966	3	780	810	1.285
91	1-Heptanol	19.24	11.3	7.9	969	970	1	889	890	50.600
92	4-Octanone	16.40	11.5	4.9	976	976	0	910	911	26.100
93	2-Ethyl-2-hexenal	17.29	11.5	5.8	976	999	23	741	742	108.000
94	1-Methylcyclooctene	18.48	11.5	7.0	976	978	2	792	841	0.810
95	Heptanonitrile	18.92	11.5	7.4	976	988	12	866	894	6.884
96	1-Octen-3-ol	19.19	11.5	7.7	976	980	4	916	919	13.200
97	3-Octanone	16.94	11.7	5.2	984	986	2	885	886	57.300

98	3,4-Dimethyl-2-cyclopenten-1-one	19.41	11.7	7.7	984	986	2	754	758	17.900
99	2-Norbornanone	19.72	11.7	8.0	984	983	1	769	835	0.445
100	2-Octanone	17.37	11.9	5.5	991	990	1	687	692	172.000
101	3,5,5-Trimethyl-2-hexene	17.70	11.9	5.8	991	985	6	706	775	7.196
102	6-Octen-2-one	18.09	11.9	6.2	991	985	6	870	896	45.700
103	3-methyl-4-Heptanol	18.25	11.9	6.4	991	997	6	752	781	2.362
104	(Methoxymethyl)-benzene	19.01	11.9	7.1	991	984	7	900	946	1.306
105	Tetrahydro-2H-pyran-2-methanol	16.35	12.1	4.3	998	992	6	792	801	1.868
106	2,6-Dimethyl-cyclohexanone	18.08	12.1	6.0	998	994	4	730	753	1.504
107	6-Methyl-5-hepten-2-one	18.19	12.1	6.1	998	986	12	685	714	38.900
108	3-Octanol	18.52	12.1	6.4	998	994	4	734	774	1.612
109	2-Octanol	18.93	12.1	6.8	998	998	0	884	897	4.796
110	1,4-Cyclohex-2-enedione	20.06	12.1	8.0	998	1032	34	758	812	11.100
111	Octanal	17.62	12.3	5.3	1005	1003	2	920	935	19.700
112	Octahydro-1H-indene	19.27	12.3	7.0	1005	991	14	674	835	0.307
113	1-(2-Methoxypropoxy)-2-propanol	20.25	12.3	8.0	1005	1010	5	712	710	0.542
114	Benzofuran	21.01	12.3	8.7	1005	1004	1	931	939	10.400
115	1-Propenyl-benzene	16.17	12.5	3.7	1012	1011	1	827	834	1.035
116	1-(1-Cyclohexen-1-yl)-ethanone	19.41	12.5	6.9	1012	1023	11	859	912	5.548
117	Cycloheptanone	20.18	12.5	7.7	1012	1015	3	872	873	68.500
118	Methyl ester heptanoic acid	17.86	12.7	5.2	1020	1023	3	789	812	0.537
119	3,5-Octadien-2-ol	18.60	12.7	5.9	1020	1038	18	788	799	1.485
120	Bicyclo[6.1.0]nonane	19.98	12.7	7.3	1020	1003	17	693	790	0.555
121	(E,E)-2,4-heptadienal	20.65	12.7	8.0	1020	1012	8	718	748	0.989
122	2,6-Dimethyl-7-octen-4-one	18.89	12.9	6.0	1027	1047	20	663	706	13.100
123	3-Ethyl-4-methylpentan-1-ol	19.11	12.9	6.2	1027	1023	4	668	705	8.291
124	Methyl-cyclooctane	19.42	12.9	6.5	1027	999	28	720	743	3.181
125	3,4,5-Trimethyl-2-cyclopenten-1-one	19.80	12.9	6.9	1027	1033	6	844	896	14.400
126	2-Ethyl-1-hexanol	20.38	12.9	7.5	1027	1030	3	845	893	2.736
127	3-Octen-2-one	19.82	13.1	6.7	1034	1040	6	727	728	23.600
128	5-Ethylcyclopent-1-enecarboxaldehyde	20.19	13.1	7.1	1034	1040	6	655	665	3.698
129	4,5-Dimethyl-2-cyclohexen-1-one	20.48	13.3	7.2	1041	1016	25	735	740	7.903
130	2,3-Dimethyl-2-cyclopenten-1-one	22.14	13.3	8.9	1041	1040	1	811	832	2.166
131	3-(1-Methylethyl)-2-	20.97	13.5	7.5	1048	1070	22	664	667	2.731

	cyclopenten-1-one									
132	1-Ethynyl-4-methyl-benzene	21.35	13.5	7.9	1048	1064	16	699	904	4.000
133	Cis-4-methylcyclohexyl ester formic acid	16.81	13.7	3.1	1055	1035	20	688	727	2.288
134	Cyclopropyl-benzene	19.12	13.7	5.4	1055	1032	23	797	831	7.864
135	2,2,3-Trimethyl-bicyclo[2.2.1]heptane	20.22	13.7	6.5	1055	1052	3	705	738	0.978
136	(E)-2-Octenal	20.36	13.7	6.7	1055	1060	5	899	910	19.300
137	1-Propynyl-benzene	21.37	13.7	7.7	1055	1052	3	782	837	0.817
138	N-butyl-benzene	19.08	13.9	5.2	1062	1054	8	834	940	0.435
139	3-Nonen-5-one	19.50	13.9	5.6	1062	1051	11	681	698	16.500
140	3-Methyl-1,2,4-cyclopentanetrione	20.72	13.9	6.8	1062	1090	28	684	716	5.003
141	2,3,4-Trimethyl-2-cyclopenten-1-one	21.63	13.9	7.7	1062	1071	9	874	906	4.541
142	2-Hexyl-tetrahydrofuran	18.84	14.1	4.7	1069	1075	6	696	724	0.491
143	Cyclohexyl ester acetic acid	20.24	14.1	6.1	1069	1043	26	681	691	21.600
144	2-Ethyl-3-methoxy-2-cyclopentenone	20.40	14.1	6.3	1069	1097	28	693	677	13.800
145	Decahydro-, trans-naphthalene	20.55	14.1	6.5	1069	1056	13	691	727	0.561
146	2-Methoxy-phenol	21.61	14.1	7.5	1069	1090	21	657	741	0.191
147	1-Octanol	21.87	14.1	7.8	1069	1071	2	909	910	46.200
148	(E)-2-Octen-1-ol	22.75	14.1	8.7	1069	1067	2	757	826	0.492
149	3-Methyl-benzaldehyde	23.63	14.1	9.5	1069	1070	1	904	931	1.879
150	2-Methyl-enzaldehyde	23.68	14.1	9.6	1069	1064	5	915	947	0.836
151	2-Hexyl-2-furanmethanol	18.86	14.3	4.6	1076	1075	1	717	728	3.263
152	5-Nonanone	19.29	14.3	5.0	1076	1073	3	742	791	7.255
153	1,2-Dimethyl-cyclooctane	20.17	14.3	5.9	1076	1069	7	682	692	6.791
154	3,7-Dimethyl-1,5,7-octatrien-3-ol	20.58	14.3	6.3	1076	1107	31	670	786	1.803
155	3-Ethyl-2,6-dimethyl-pyridine	18.24	14.5	3.7	1083	1110	27	685	709	0.435
156	8-Nonen-2-one	20.77	14.5	6.3	1083	1085	2	843	874	77.700
157	2(1H)-Pyridinone	21.63	14.5	7.1	1083	1094	11	658	747	2.423
158	Octanenitrile	21.75	14.5	7.3	1083	1082	1	885	907	3.066
159	3-Nonanone	19.86	14.7	5.2	1090	1090	0	777	894	3.646
160	2-Nonanone	20.26	14.7	5.6	1090	1092	2	817	825	109.000
161	4,4-Dimethyl-2-cyclohexen-1-one	22.46	14.7	7.8	1090	1101	11	785	839	3.304
162	Undecane	18.20	14.9	3.3	1097	1100	3	847	896	0.807

163	3,3,6-Trimethyl-1,5-heptadien-4-ol	19.27	14.9	4.4	1097	1084	13	732	776	0.971
164	7-Methyl-3-octen-2-one	21.44	14.9	6.5	1097	1062	35	693	758	2.395
165	Linalool	22.01	14.9	7.1	1097	1099	2	828	836	1.679
166	Acetophenone	22.51	14.9	7.6	1097	1065	32	928	931	40.900
167	Nonanal	20.53	15.1	5.4	1105	1104	1	904	909	8.493
168	2-Methyl-3-ethyl-2-heptene	21.31	15.1	6.2	1105	1073	32	659	765	0.496
169	Methyl ester 4-octenoic acid	21.13	15.3	5.8	1112	1118	6	731	779	4.368
170	4-Acetyl-1-methylcyclohexene	22.14	15.3	6.8	1112	1137	25	748	752	2.667
171	1,2,3,5-Tetramethyl-benzene	23.18	15.3	7.9	1112	1117	5	687	711	1.579
172	2-Methyl-benzofuran	23.63	15.3	8.3	1112	1109	3	801	887	0.846
173	Methyl ester octanoic acid	20.72	15.5	5.2	1119	1126	7	889	900	6.187
174	2-Nonanol	21.17	15.5	5.7	1119	1102	17	652	679	5.060
175	Decahydro-, cis-naphthalene	22.30	15.5	6.8	1119	1101	18	712	722	3.222
176	2-Nonen-4-one	21.92	15.7	6.2	1126	1124	2	684	731	1.410
177	2-Propyl-cyclohexanone	22.53	16.1	6.4	1141	1135	6	761	765	17.000
178	4-Isopropenylcyclo hexanone	23.30	16.1	7.2	1141	1161	20	706	772	0.502
179	2,4,6-Cycloheptatrien-1-one	21.08	16.3	4.8	1148	1182	34	730	790	73.100
180	Cyclodecane	23.03	16.3	6.7	1148	1147	1	714	750	1.782
181	β-Methyl-benzeneethanol	21.14	16.5	4.6	1155	1179	24	670	671	16.700
182	(E)-2-Nonenal	23.15	16.5	6.7	1155	1162	7	846	865	2.408
183	6,6-Dimethyl-(1R)-bicyclo[3.1.1]heptan-2-one	24.12	16.7	7.4	1163	1139	24	707	742	1.644
184	1,2,3,4-Tetrahydro-naphthalene	23.65	16.9	6.8	1170	1155	15	888	929	1.556
185	trans-3-Nonen-2-one	23.88	16.9	7.0	1170	1144	26	764	780	3.444
186	1-Nonanol	24.42	16.9	7.5	1170	1173	3	668	805	1.315
187	3-Nonen-2-one	23.05	17.1	6.0	1177	1142	35	661	669	3.809
188	1,2-Dimethyl-3-(1-methylethenyl)-, [1R-(1α,2α,3α)]-cyclopentanol	23.27	17.1	6.2	1177	1155	22	707	725	2.690
189	5-Methyl-2-(1-methylethyl)-, (1α,2α,5β)-cyclohexanol	24.56	17.1	7.5	1177	1168	9	791	880	0.656
190	1-(4-Methylphenyl)-ethanone	26.58	17.1	9.5	1177	1183	6	928	960	5.038
191	2-Decanone	23.04	17.5	5.5	1192	1193	1	904	910	35.600
192	Stereoisomer p-menth-8-en-1-ol	23.79	17.5	6.3	1192	1161	31	706	727	4.517

193	Naphthalene	26.80	17.5	9.3	1192	1182	10	941	945	8.763
194	1-(2-Methylphenyl)-ethanone	27.06	17.5	9.6	1192	1173	19	773	930	0.530
195	Dodecane	21.03	17.7	3.3	1199	1200	1	665	763	0.461
196	Decanal	23.33	17.9	5.4	1206	1206	0	883	899	2.005
197	3-Decen-2-one	24.19	17.9	6.3	1206	1233	27	701	714	3.594
198	2,4-Dimethyl-benzenemethanol	25.27	18.1	7.2	1214	1226	12	661	663	55.500
199	N,N-Diethyl-2-methyl-benzenamine	24.24	18.3	5.9	1222	1193	29	778	797	0.699
200	3-(1-Methylethyl)-phenol	26.56	18.3	8.3	1222	1228	6	668	702	3.156
201	Isopropyl ether (3-methylphenyl) methanol	21.81	18.5	3.3	1229	1212	17	659	705	0.687
202	2,3,6-Trimethyl-phenol	24.79	18.5	6.3	1229	1239	10	662	669	113.000
203	3-Phenylpropanol	24.78	18.9	5.9	1244	1232	12	671	765	110.000
204	2-Ethyl-6-methyl-phenol	26.80	18.9	7.9	1244	1236	8	728	798	4.845
205	2,3-Dihydro-benzofuran	23.69	19.3	4.4	1260	1224	36	764	813	1.012
206	(E)-2-Decenal	25.82	19.3	6.5	1260	1263	3	902	914	5.968
207	N,N-Diethyl-3-methyl-benzenamine	26.30	19.3	7.0	1260	1290	30	816	849	1.491
208	4-Ethyl-3-methyl-phenol	26.97	19.3	7.7	1260	1237	23	660	748	3.114
209	(1-Methylenebutyl)-benzene	27.86	19.3	8.6	1260	1236	24	711	733	7.123
210	1-(4-Ethylphenyl)-ethanone	28.60	19.5	9.1	1267	1277	10	761	852	0.600
211	2,3,5-Trimethyl-phenol	24.94	19.9	5.0	1282	1276	6	655	655	16.100
212	3-Undecanone	25.30	19.9	5.4	1282	1283	1	715	783	2.014
213	1,3,5,5-Tetramethyl-1,3-cyclohexadiene	25.58	19.9	5.7	1282	1292	10	682	715	4.688
214	(Z)-Undec-6-en-2-one	26.13	19.9	6.2	1282	1274	8	759	805	7.867
215	1-Chloro-decane	27.13	19.9	7.2	1282	1262	20	729	752	1.423
216	3-Phenyl-2-propenal	23.44	20.1	3.3	1290	1274	16	673	783	0.679
217	2-Undecanone	25.69	20.1	5.6	1290	1294	4	927	927	9.546
218	Methyl ester decanoic acid	26.05	20.9	5.2	1321	1325	4	869	921	2.297
219	N,N-Diethyl-4-methyl-benzenamine	25.21	21.7	3.5	1353	1343	10	807	824	1.048
220	1-Undecanol	31.26	22.3	9.0	1376	1371	5	827	899	2.958
221	3-Dodecanone	27.86	22.5	5.4	1384	1385	1	780	885	0.954
222	2-Dodecanone	28.26	22.5	5.8	1384	1396	12	870	922	4.299
223	2-Methyl-2-phenylethyl ester propanoic acid	30.77	22.7	8.1	1392	1396	4	835	892	1.813
224	Decyl ester acetic acid	29.78	23.3	6.5	1417	1408	9	710	783	1.337
225	Trifluoro-dodecyl ester acetic acid	31.84	23.3	8.5	1417	1432	15	724	795	1.107
226	Methyl-3-methylphenyl	30.10	23.7	6.4	1435	1465	30	845	848	7.564

	ester carbamic acid									
227	1-Pentadecene	28.83	24.9	3.9	1487	1492	5	861	887	3.453
228	4-Phenoxy-octane	29.97	24.9	5.1	1487	1464	23	712	742	3.583
229	2-Tridecanone	31.15	24.9	6.3	1487	1497	10	683	738	1.048
230	α Isomethyl ionone	32.08	24.9	7.2	1487	1480	7	756	783	1.675
231	1-Dodecanol	29.13	25.1	4.0	1495	1473	22	656	873	0.964
232	Methyl ester dodecanoic acid	31.44	25.5	5.9	1513	1526	13	828	864	2.829
233	Dodecyl ester formic acid	29.11	25.9	3.2	1531	1543	12	698	860	1.373
234	3,5-Dimethyl-, methylcarbamate phenol	32.41	26.3	6.1	1549	1564	15	718	781	0.479
235	2,6,10-Trimethyl-tetradecane	34.67	26.5	8.2	1558	1539	19	679	734	0.715

$^{1}t_R$ = the retention time on ^{1}D column $^{2}t_R$= the retention time on ^{2}D column
$I_{Experiment}$ = Retention index from experiment $I_{Literature}$ = Retention index from literature
$^{1}t_R + {}^{2}t_R$ = total of the retention time on ^{1}D and ^{2}D column or peak time observed with MS detector

Table S4. Experimental profile of compounds in the oxidized products in water obtained using the Rancimat method and the analysis using 1 injection, with the compound identification performed by auto integration using Mass Hunter.

Order	Name	Retention time (min)	Match	R match
1	n-Hexane	6.51	852	860
2	2-Butanone	7.77	888	932
3	2-Pentanone	9.25	825	839
4	3-Methyl-butanal	9.34	763	766
5	Toluene	11.02	878	887
6	3-Hexanone	11.25	866	919
7	2-Hexanone	11.65	832	838
8	Octanal	11.80	715	719
9	5-Hexen-2-one	12.15	887	894
10	4-Methyl-3-penten-one	12.55	874	885
11	3,4,5-Trimethyl-1-hexene	12.84	755	776
12	3-Methyl-4-penten-2-one	13.20	819	942
13	But-3-en-1-yl propyl carbonate	13.28	720	761
14	Tetrahydrofurfuryl acrylate	13.47	726	773
15	4-Methyl- ,(S)-1-hexanol	13.89	790	797
16	4-Methyl-5-nonanone	14.04	738	818
17	2-Methyl-cyclopentanone	14.15	846	874
18	3-Hexen-2-one	14.27	857	865
19	1-Methyl-cyclohexanol	14.44	753	757
20	(Z)-2-Heptene	14.57	743	756
21	Heptanal	14.64	731	790

22	1,5-Dimethyl-6-oxa-bicyclo[3.1.0]	14.81	765	789
23	alpla-Methylstyrene	15.00	828	842
24	3-Methyl-3-phenyl-azetidine	15.12	686	903
25	2-Ethyl-4-methyl-1-pentanol	15.27	678	751
26	1,5-Dimethyl-6-oxa-bicyclo[3.1.0]hexane	15.33	788	798
27	1,5-Dimethyl-6-oxa-bicyclo[3.1.0]hexane	15.58	780	790
28	5-Methyl-3-hexanol	15.78	808	878
29	2-Butyltetrahydro-furan	15.85	791	847
30	5-Methyl-3-hexen-2-one	16.02	808	818
31	Hexanenitrile	16.07	747	800
32	2-nonanol	16.21	760	792
33	2,2-Dimethyl-,(Z)-3-hexene	16.29	815	887
34	4-Octanol	16.37	893	904
35	Cyclooctane	16.56	742	753
36	3,4,5-Trimethyl-1-hexene	16.67	751	794
37	(Z)-3-Hepten-2-one	16.80	830	835
38	2-Ethyl-cyclopentanone	16.91	780	811
39	5-Methyl-3-heptanone	16.92	752	753
40	5-Methyl-3-heptanone	16.94	795	800
41	3-Isoproylcyclopentene	17.13	755	777
42	1-(2-Butenenyloxy)-, (E)-heptane	17.22	711	773
43	1-Cyclohexyl-ethanone	17.29	780	781
44	4-Hydroxy-4-methyl-cyclohexanone	17.37	768	784
45	7-Octen-2-one	17.41	710	737
46	Propyl-cyclopentane	17.44	825	843
47	2,4-Dimethyl-cyclohexanol	17.63	816	833
48	3-t-Butyl-oct-6-en-ol	17.69	742	746
49	1-Methyl-7-oxabicyclo[4.1.0]heptane	17.85	762	819
50	1,5-Dimethyl-7-oxabicyclo[4.1.0]heptane	17.94	812	813
51	1,5-Dimethyl-7-oxabicyclo[4.1.0]heptane	18.09	784	786
52	1-Cyclohexyl-ethanone	18.19	828	878
53	(Z)-6-octen-2-one	18.41	861	864
54	4-Methyl-dodec-33-en-1-ol	18.53	717	726
55	2-Methyl-oct-2-enedial	18.67	757	768
56	Undecanal	18.77	762	767
57	Tetradecyl-oxirane	18.86	753	766
58	n-Heptadecanol-1	18.99	752	752
59	1,2,4-Trimethyl-cyclohexane	19.11	734	766
60	5,9-Dimethyl-1-decanol	19.19	749	762
61	1-nonanol	19.24	799	808
62	Hexyl-oxirane	19.25	796	807
63	Hexyl-oxirane	19.26	734	762
64	3,5-Dimethyl-cyclohexene	19.41	785	807

65	[(dodecyloxy)methyl]-oxirane	19.50	741	746
66	(z)-2,3-Dimethyl-3-heptane	19.71	769	782
67	undecanal	19.82	708	711
68	2-Ethyl-cyclohexanone	19.95	886	913
69	Hexadecahydro-cyclobuta[1,2,3,4]dicyclooctene	20.06	762	774
70	2,3-Dimethyl-2-cyclopenten-1-one	20.11	799	852
71	Cyclodecane	20.19	788	793
72	1,2-Epoxynonane	20.26	750	764
73	(E)-2-Octenal	20.36	827	842
74	trans-3-Nonen-2-one	20.41	793	803
75	4,5-Dimethyl-2-cyclohexen-1-one	20.47	778	848
76	Dodecanal	20.54	785	795
77	Nona-3,5-dien-2-ol	20.64	792	796
78	3-Propyl-, (2Z)-2,4-pentadien-1-ol	20.72	714	784
79	Nona-3,5-dien-2-ol	20.77	756	762
80	2-Methylbenzo(e) [1,3]oxathiane	21.05	607	664
81	4-Ethynyl-6,8-dioxabicyclo[3.2.1]oct-2-en-4-ol	21.06	620	664
82	3-Propyl-, (2Z) -2,4-pentadien-1-ol	21.23	699	802
83	4-Chloro-3-n-butyltetraahydropyran	21.35	602	675
84	Nona-3,5-dien-2-ol	21.46	745	756
85	1-Methyl-3-cyclohexene-1-carboxaldehyde	21.63	714	746
86	Tetradecyl-oxirane	21.75	742	812
87	Methyl octyl ester carbonic acid	21.87	777	835
88	7-Oxo-octanoic acid	22.03	711	713
89	Levomenthol	22.14	776	818
90	Levomenthol	22.29	739	763
91	Cyclononanone	22.52	757	760
92	Mannosamine	22.66	647	648
93	Benzamidine	22.77	664	682
94	(1R,3E,7E,11R)-1,5,5,8-Tetramethyl-12-oxabicyclo[9.1.0]dodeca-3,3-diene	22.94	636	703
95	4-[[(2-Methoxy-4-octadecenyl)oxy)methyl]-2,2-dimethyl-1,3-dioxolane	23.04	684	705
96	2,4-Dimethyl-3-heptanol	23.08	689	707
97	I-Gala-I-ido-octose	23.15	695	724
98	1-(1-Cyclohexen-1-yl)-ethanone	23.26	744	767
99	10-Undecanal	23.33	755	761
100	4-Cyclohexyl-2-butanone	23.51	704	803
101	1-(1-Methoxypropan-2-yloxy)propan-2-yl acetate	23.63	626	738
102	Z,Z-2,5-Pentadecadien-1-ol	23.74	702	706
103	3-Ethoxy-3,7-dimethyl-1,6-octadiene	23.84	687	700
104	Methyl ester 6-nonenoic acid	23.84	797	846
105	Acetophenone	24.08	739	798

106	Z,Z,Z-1,4,6,9-Nonadecatetraene	24.19	686	687
107	alpha,alpha-Dimethyl-benzenemethanol	24.75	778	795
108	12-15,16-Diepoxyhexadecane	25.26	701	701
109	2-undecanone	25.69	752	875
110	4-tert-Butylcyclohexyl acetate	25.76	800	829
111	3-Ethoxy-3,7-dimethyl-1,6-octadiene	25.85	681	698
112	E-2-Hexenyl benzoate	26.02	701	707
113	4-Acetonylcycloheptanone	26.13	716	731
114	2-Methyl-1-hexadecanol	26.29	738	738
115	4-Trifluroacetoxytridecane	26.33	799	839
116	11-Hydroxy-, methyl ester, [s-(E)]-8-dodecenoic acid	26.33	728	731
117	1-(3-Methylphenyl)-ethanone	26.58	731	799
118	Tetrahydro-4-hydroxy-6-pentyl-2H-pyran-2-one	26.66	664	707
119	Naphthalene	26.80	700	836
120	Bis(tert-butyldimethylsily)ether 3-chloropropane-1,2-diol	27.86	649	727
121	Geranyl vinyl ether	27.93	707	719
122	2-Dodecanone	28.26	757	871
123	[(Hexadecyloxy)methyl]-oxirane	28.75	719	769
124	3-Trifluroacetoxypentadecane	28.83	763	796
125	3-Trifluroacetoxydodecane	28.92	732	757
126	N-carbobenzyloxy-l-tyrosyl-l-valine	30.10	727	788
127	Octaethylene glycol monododecyl ether	31.33	740	741
128	Pterin-6-carboxylic acid	32.01	654	666
129	Octaethylene glycol monododecyl ether	34.33	700	702
130	Eicosane	34.71	877	891

Peak capacity approximation based on the undersampling approach

When the significantly wide H/C window (0.2 min) was applied in this study, undersampling process occurred in the data analysis [19]. This results in re-combination of the separated peaks from ^{1}D separation (^{1}D resolution loss due to overlapped selectivity with the ^{2}D separation) within the same H/C fraction. In an extreme case, such process leads to the average peak width at baseline in ^{1}D separation ($^1w_{b,ave}$) = $t_{H/C}$ as previously reported in [3]. In general, $^1w_{b,ave}$ of peaks can be approximated according to[1]

$$^1w_{b,ave} = \langle\beta\rangle w_{b,ave,\,MDGC\,-\,FID} \tag{S1}$$

where $<\beta>$ is the average first-dimension broadening factor (during the sampling process resulting in broader peak in ^{1}D separation than the corresponding width in 1DGC). $<\beta>$ can be approximated as [19]

$$\langle\beta\rangle = \left[\sqrt{1 + 0.21\left(\frac{t_{H/C}}{\sigma_{ave,\,MDGC\,-\,FID}}\right)^2}\right] \tag{S2}.$$

$w_{b,ave,MDGC–FID}$ and $\sigma_{ave,MDGC–FID}$ are average peak width at baseline and peak standard deviation of all the separated peaks (excluding that of the solvent) obtained from MDGC analysis with the DS diverging flow towards FID. The average width at baseline in chromatograms obtained with MS for each H/C analysis was assumed to be $^2w_{b,ave}$ obtained from MDGC analysis with the DS diverging flow towards MS.

$n_{c,total}$[20] is calculated based on the 2D rectangular separation space between the first and the latest eluting peaks with the retention times of $t_{R,first}$ and $t_{R,last}$, respectively. $n_{c,total}$ was calculated here according to [19]

$$n_{c,total} = {}^1n_c \times {}^2n_c \tag{S3}$$

$$^1n_c = 1 + \frac{^1t_{R,last} - {}^1t_{R,first}}{\langle\beta\rangle w_{b,ave,\,MDGC\,-\,FID}} \tag{S4}$$

$$^{2}n_c = \frac{^{2}D\ separation\ time}{^{2}w_{b,ave}} \quad \text{(S5)}$$

where the superscripts 1 and 2 indicate that the parameters are in ^{1}D or^{2}D separation, respectively. ^{2}D separation time of 5 min was applied in this study since 2D separation was performed under wraparound situation where the ^{2}D separation space can be fully occupied. It should be noted that **Equations S1-S5** were used for the n_c calculation. However, these equations can be applicable providing that (1) the sample contains 50-1000 constituents, (2) ^{1}D to ^{2}D peak capacity ratios ($^{1}n_c/^{2}n_c$) within the range from 0.125 to 8, (3) reduced $^{1}\sigma$ to reduced $^{2}\sigma$ ratios of ≥1 and ≤8, and (4) saturation of the separation space (α) of ≤1.5 where α is a statistical parameter inversely proportional to the total peak capacity ($n_{c,total}$)[19]. Whilst most of the data were in agreement with the criteria above, the n_c calculation for the CH/C using 2.5 and 5.0 min windows can be less reliable due to the relatively high α and reduced σ ratio data, see all the related data provided in **Table S5**. The calculated peak capacity data obtained by using the undersampling approach (**Equations S1-S5**) are provided in **Figure S2**.

Table S5. Data of parameters related to peak capacity approximation for the CH/C analysis of the oxidized products in sample (obtained using the Rancimat method) using different H/C window. The data not passing the criteria are shown in *red italic*.

H/C window	<β>	Approximated saturation of the separation space (α)	Reduced $^{1}\sigma$	Reduced $^{2}\sigma$	Reduced σ Ratio	$^{1}n_c$/<β>	$^{2}n_c$	n_c Ratio	Total n_c	# identified peaks
0.20	1.25	1.00	0.001	0.006	6.08	190	40	0.21	7600	235
0.25	1.37	1.03	0.001	0.007	6.27	174	39	0.22	6786	228
0.33	1.60	1.05	0.001	0.007	6.71	149	37	0.25	5513	223
0.42	1.85	1.07	0.001	0.008	7.18	129	34	0.26	4386	220
0.50	2.12	1.08	0.001	0.008	7.39	113	33	0.29	3729	217
0.83	3.27	1.16	0.001	0.008	7.58	74	33	0.45	2442	202
1.00	3.87	1.19	0.001	0.008	7.68	62	32	0.52	1984	197
1.25	4.78	1.29	0.001	0.008	7.92	51	31	0.61	1581	182
1.67	6.32	1.37	0.001	0.008	*8.01*	39	31	0.79	1209	172
2.50	9.41	*1.57*	0.001	0.009	*8.20*	27	30	1.11	810	150
5.00	18.73	*1.81*	0.001	0.009	*8.30*	14	30	2.14	420	130
Suggested criteria for the		***<=1.5***			***1<= and***			***0.125<=***		***50-1000***

capacity calculation[1]		*<=8*	*and <=8*

[1]With the approach obtained from J. M. Davis, D. R. Stoll and P. W. Carr, *Anal. Chem.,* 2008, **80**, 461-73.

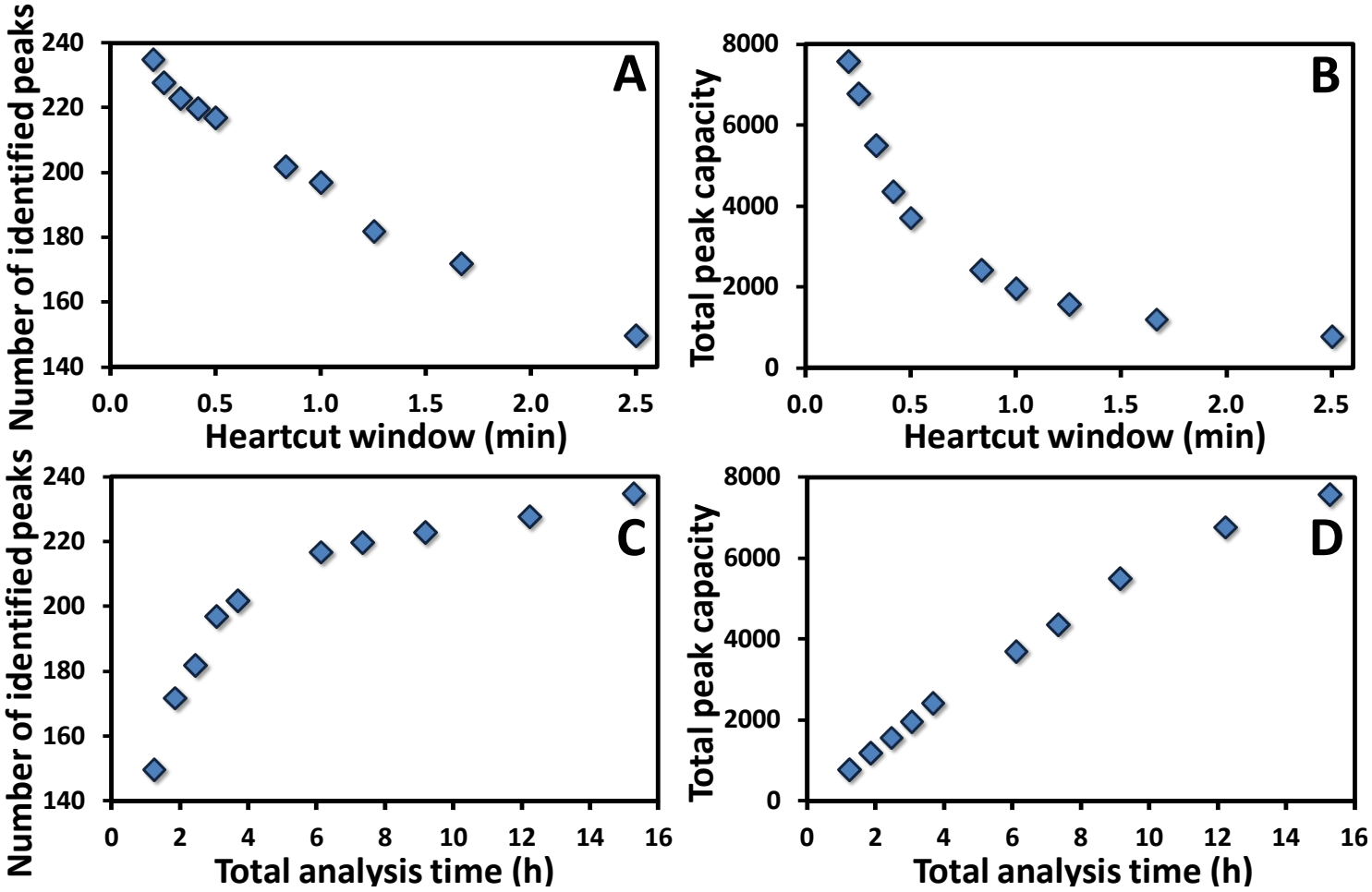

Figure S2. Effect of heartcut window with the developed CH/C MDGC analysis on (A) number of separated peaks and (B) total peak capacity obtained according to the undersampling approach, with the corresponding plots of (C) total analysis time vs number of separated peaks and (D) total analysis time vs total peak capacity.