Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.

Supplementary materials for

Comparative study of naproxen degradation by the UV/chlorine and the UV/ H_2O_2 advanced oxidation processes

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Number of figures: 7

Number of texts: 2

Number of tables:6

Lists of captions of Texts, Figures and Tables

Text S1. The operating conditions of UPLC-QTOF MS under ESI negative mode.

The chromatographic separation was achieved using a C-18 column (Waters acquity BEH, 1.7 μm). The mobile phase consisted of 0.1% formic acid water (A) and methanol (B), with a gradient elution of A/B from 95/5 (v/v) to 5/95 for 20 min. The sample injection volume was 0.3 μL. The Ion Mobility-Q-TOFMS was operated under the following conditions: ESI negative mode, capillary 2.5 kV, source temperature 110 °C, desolvation temperature 350 °C, sampling cone 30 V, cone gas flow 30 L/Hr, desolvation gas flow 700 L/Hr, nebulizer gas flow 6 bar, trap collision energy 4 eV, transfer collision energy 2 eV, trap gas flow 2 mL/min, lock spray capillary 2.5 kV, collision energy 4 eV, trap MSMS collision energy ramp 4~30eV.

Text S2. The calculation of EE/O.

Electrical Energy per Order (EE/O) was applied to compare the cost of the UV/chlorine and UV/H_2O_2 AOPs for the removal of 90% NPX. The total EE/O includes electrical energy for UV irradiation (EE/O_{UV}) and equivalent electrical energy for oxidant consumption ($EE/O_{oxidant}$). The calculation of EE/O, EE/O_{UV} and $EE/O_{oxidant}$ followed eqs s1-s4.

$$EE/O = EE/O_{UV} + EE/O_{oxidant}\ (\mathrm{kWh/m^3}) \tag{S1}$$

$$EE/O_{UV} = \frac{Pt * 1000}{V * \log([NPX]t/[NPX]0}\ (\mathrm{kWh/m^3}) \tag{S2}$$

$$EE/O_{oxidant} = Eq_{oxidant} * Oxidant/O\ (\mathrm{kWh/m^3}) \tag{S3}$$

$$Oxidant/O = \frac{[Oxidant]0}{\log([NPX]t/[NPX]0}\ (\mathrm{mg/L}) \tag{S4}$$

where EE/O_{UV}, and $EE/O_{oxidant}$ are the electrical energy consumptions by UV irradiation and oxidant (chlorine or H_2O_2), respectively, $\mathrm{kWh/m^3}$; P is electronic energy input of UV lamps, kW (photoelectric conversion efficiency of the reactor was 25.0%, P = UV irradiance / 25.0%) [s1]; V is the reaction volume, L; t is the reaction time, h; $[NPX]_0$ and $[NPX]_t$ are the NPX concentrations at 0 h and t h, respectively, mg/L; $[Oxidant]_0$ is the concentration of oxidant, mg/L, $Eq_{oxidant}$ is the equivalent electric energy consumption to produce per milligram of oxidant, kWh/mg ($Eq_{chlorine} = 11.6 \times 10^{-6}$ kWh/mg [s2], $Eq_{H2O2} = 10.8 \times 10^{-6}$ kWh/mg [s3]); Oxidant/O is the oxidant required for per order magnitude elimination of NPX, mg/L).

Table S1. Reactivities between scavengers and involved radicals in the processes.

Scavenger	Rate constants (M^{-1} s^{-1})				
	HO•	Cl•	ClO•	$Cl_2^{\bullet-}$	$CO_3^{\bullet-}$
HCO_3^-	8.5×10^6 [s4]	2.2×10^8 [s5]	600 [s5]	8.0×10^7 [s6]	-
TBA	6.0×10^8 [s4]	3.0×10^8 [s7]	1.3×10^7 [s9]	700 [s8]	9.6×10^4 [s9]

Table S2. Concentrations of HOCl and OCl^- at different pHs with 50 μM chlorine dosage.

pH	HOCl (μM)	OCl^- (μM)
6	48.5	1.5
7	38	12
9	1.5	48.5

Table S3. Simulated molar concentration of reactive species with different bicarbonate dosages

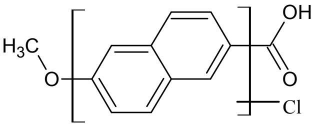
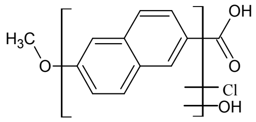
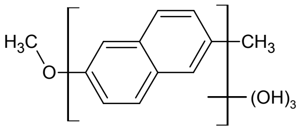
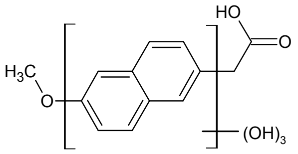
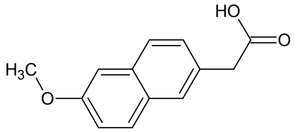
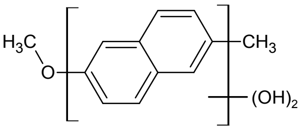
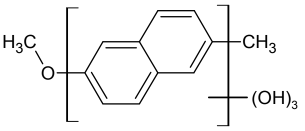
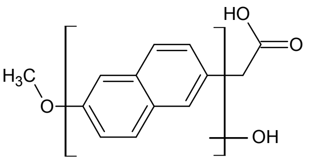
Water treatment	dosage	$CO_3^{\bullet -}$ (M)	HO• (M)	Cl• (M)	$Cl_2^{\bullet -}$ (M)	ClO• (M)
UV/H_2O_2	control	1.62×10^{-13}	9.40×10^{-14}	0	0	0
	1 mM	2.45×10^{-12}	8.05×10^{-14}	0	0	0
	5 mM	7.42×10^{-12}	5.11×10^{-14}	0	0	0
UV/chlorine	control	4.74×10^{-12}	9.28×10^{-14}	2.83×10^{-14}	1.82×10^{-13}	9.00×10^{-13}
	1 mM	1.65×10^{-11}	7.59×10^{-14}	1.56×10^{-14}	4.57×10^{-14}	6.83×10^{-13}
	5 mM	2.02×10^{-11}	3.94×10^{-14}	7.65×10^{-15}	7.04×10^{-15}	5.05×10^{-13}

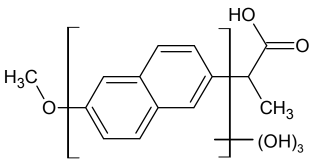
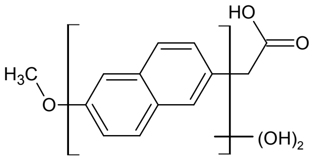
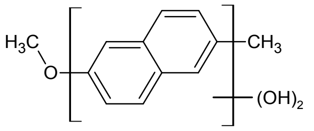
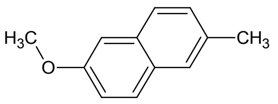
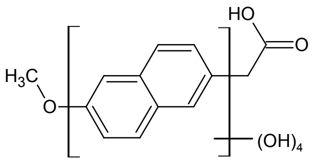
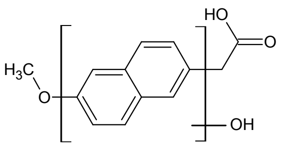
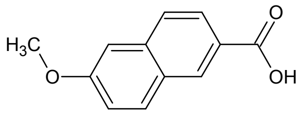
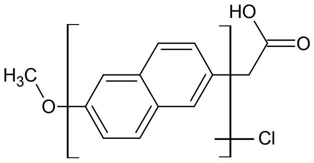
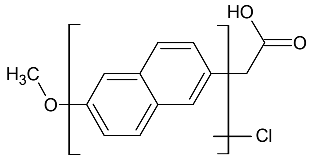
Table S4. Water quality parameters of the real water sample.

	NH_4^+	Mg^{2+}	Ca^{2+}	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	HCO_3^-	DOC
Concentration (mg/L)	0.04	n.d.	33.13	0.44	16.03	0.06	n.d.	10.79	58.56	0.628

Note: n.d. means undetectable.

Table S5. Accurate mass measurement of product ions of NPX and its transformed products as determined by HPLC/ESI-IT-TOFMS.

Compound	RT (min)	$[M\text{-}H]^-$ (m/z)		Elemental formula	Proposed Structure	UV/chlorine	UV/H_2O_2
		Theoretical	Experimental				
236	1.865	235.0150	235.0162	$C_{12}H_8O_3Cl$		√	
252	2.168	251.0101	251.0111	$C_{12}H_8O_4Cl$		√	
220[a]	2.691	219.0649	219.0657	$C_{12}H_{11}O_4$			√
264	3.915	263.0544	263.0556	$C_{13}H_{11}O_6$			√
216	4.642	215.0692	215.0708	$C_{13}H_{11}O_3$		√	√
204[a]	5.102	203.0689	203.0708	$C_{12}H_{11}O_3$			√
220[b]	5.384	219.0644	219.0657	$C_{12}H_{11}O_4$			√
232[a]	5.622	231.0647	231.0657	$C_{13}H_{11}O_4$		√	√

278	5.862	277.0705	277.0712	$C_{14}H_{13}O_6$		√	√
248	5.918	247.0597	247.0606	$C_{13}H_{11}O_5$		√	√
204[b]	5.917	203.0711	203.0708	$C_{12}H_{11}O_3$			√
172	6.341	171.0805	171.0810	$C_{12}H_{11}O$			√
280	6.576	279.0499	279.0505	$C_{13}H_{11}O_7$			√
232[b]	8.051	231.0650	231.0657	$C_{13}H_{11}O_4$		√	√
202	8.541	201.0556	201.0552	$C_{12}H_9O_3$		√	√
250[a]	8.734	249.0312	249.0318	$C_{13}H_{10}O_3Cl$		√	
250[b]	9.028	249.0309	249.0318	$C_{13}H_{10}O_3Cl$		√	

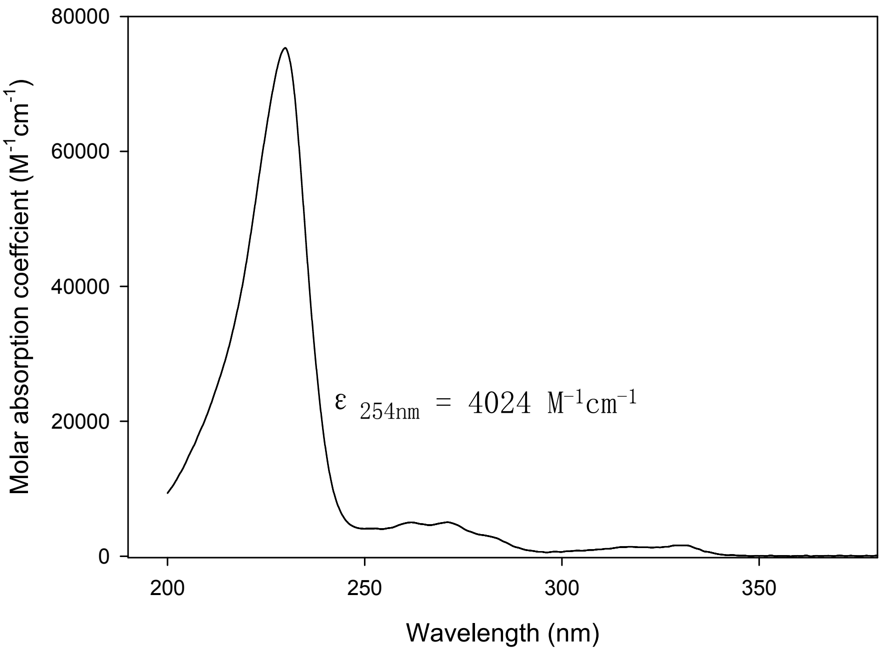


Figure S1. UV-vis absorption spectrum of NPX in aqueous phase.

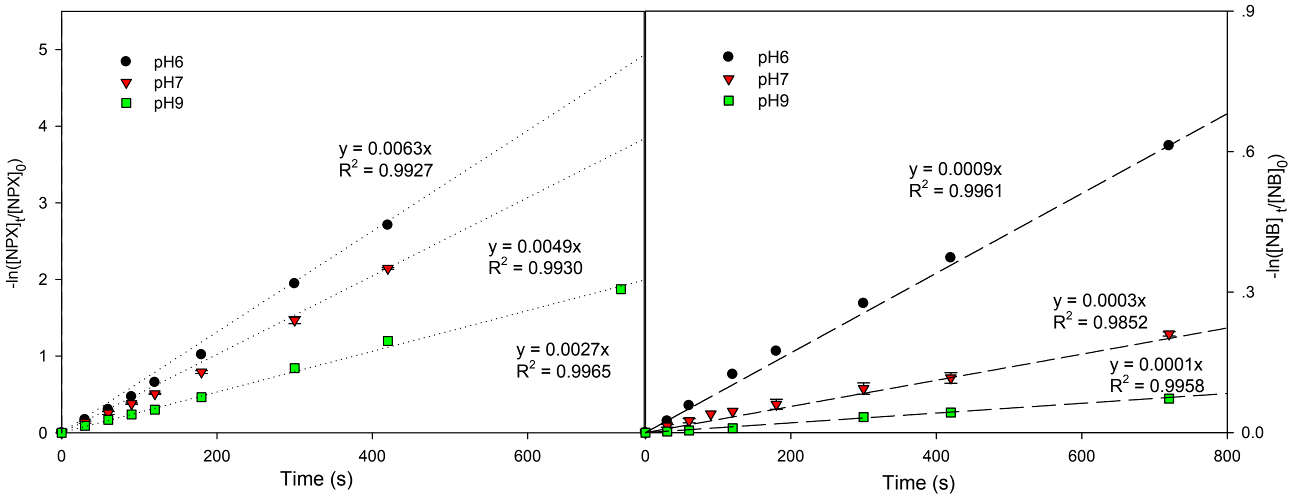


Figure S2. Degradation of NPX and NB by UV/chlorine AOP in pure water at different pHs. Conditions: $[\text{chlorine}]_0$ = 50 μM, $[\text{NPX}]_0$ = 5 μM, $[\text{NB}]_0$ = 1 μM, $[\text{Phosphate buffer}]_0$ = 2 mM.

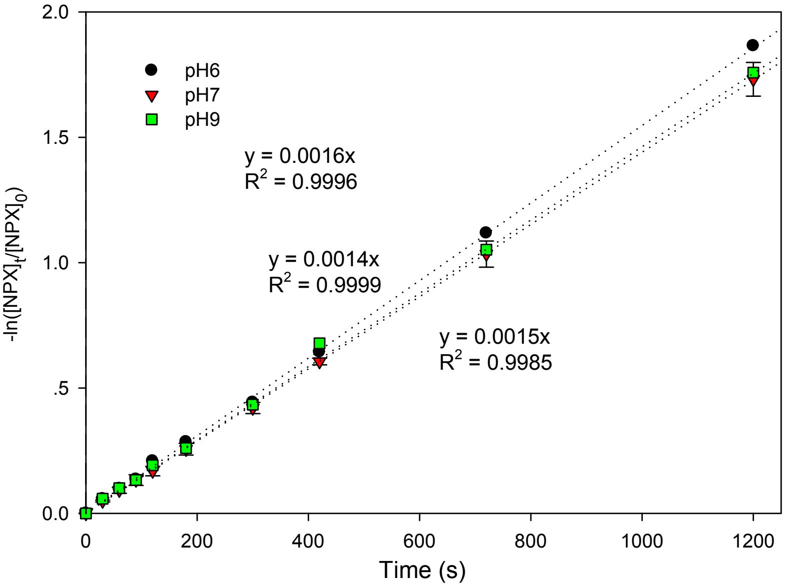


Figure S3. Degradation of NPX by the UV/H_2O_2 AOP in pure water at different pHs. Conditions: $[H_2O_2]_0$ = 50 μM, $[NPX]_0$ = 5 μM, $[\text{phosphate buffer}]_0$ = 2 mM.

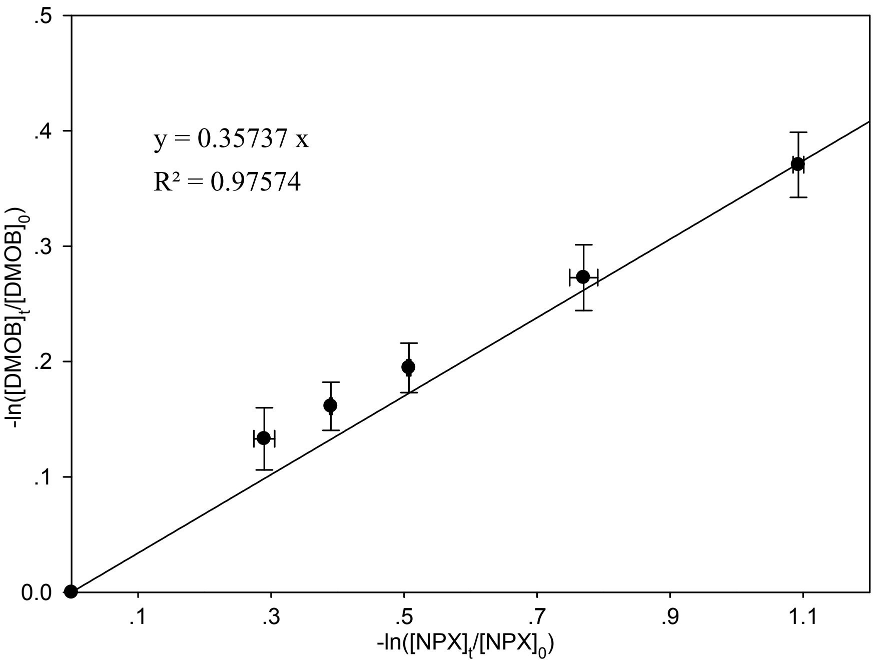


Figure S4. Competition kinetics of NPX versus the reference compound DMOB at pH 10 by ClO•. Direct UV photolysis and chlorination have been subtracted. Conditions: $[\text{chlorine}]_0$ = 300 μM, $[\text{NPX}]_0$ = $[\text{DMOB}]_0$ = 5 μM. $[\text{TBA}]_0$ = 0.5 mM.

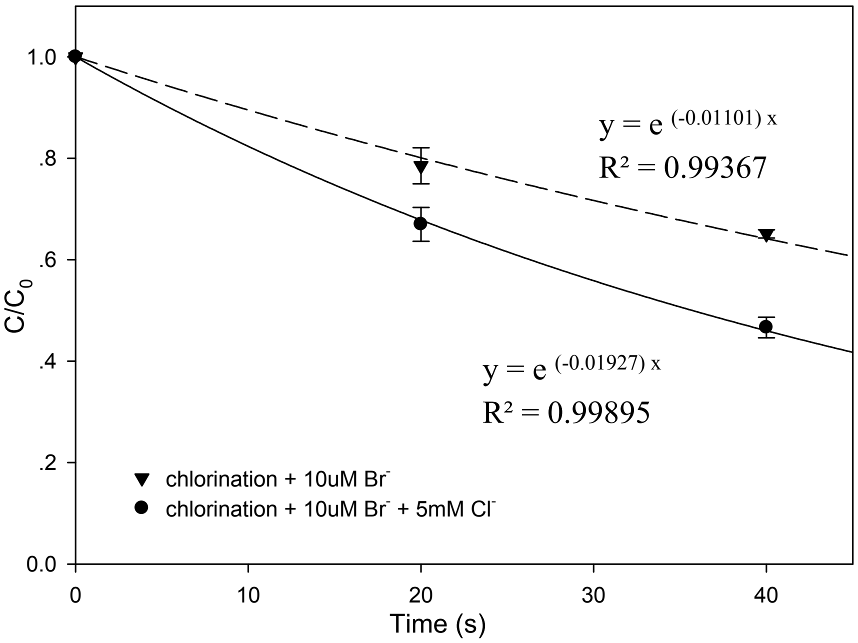


Figure S5. The degradation kinetics of NPX by chlorination with addition of bromide and chloride in pure water at pH 7. Conditions: $[\text{chlorine}]_0$ = 50 μM, $[\text{NPX}]_0$ = 5 μM, $[\text{bromide}]_0$ = 10 μM, $[\text{chloride}]_0$ = 5 mM.

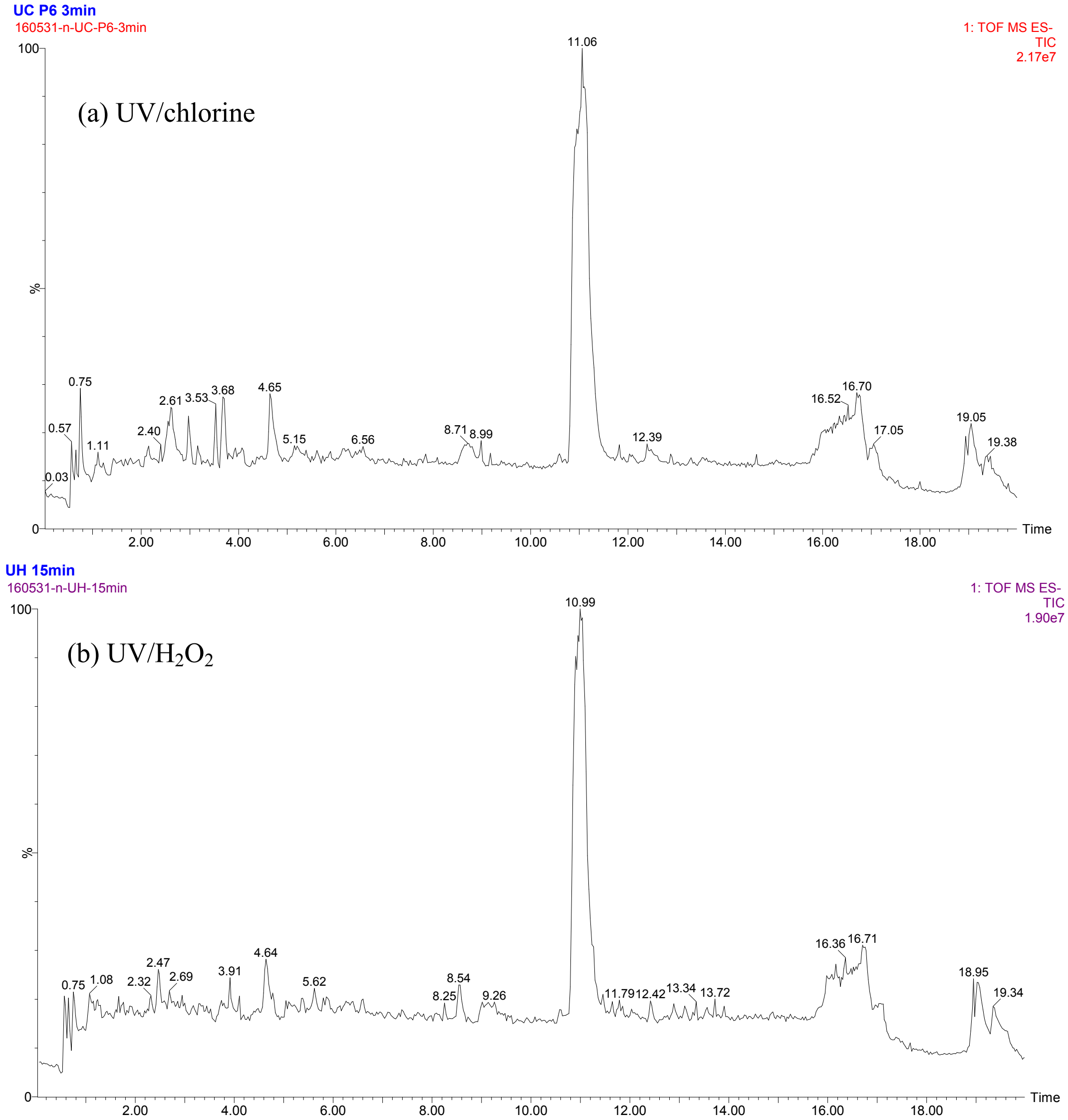
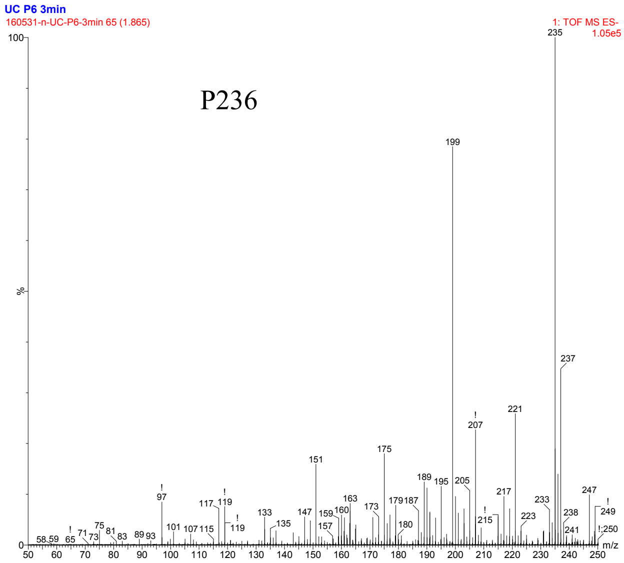
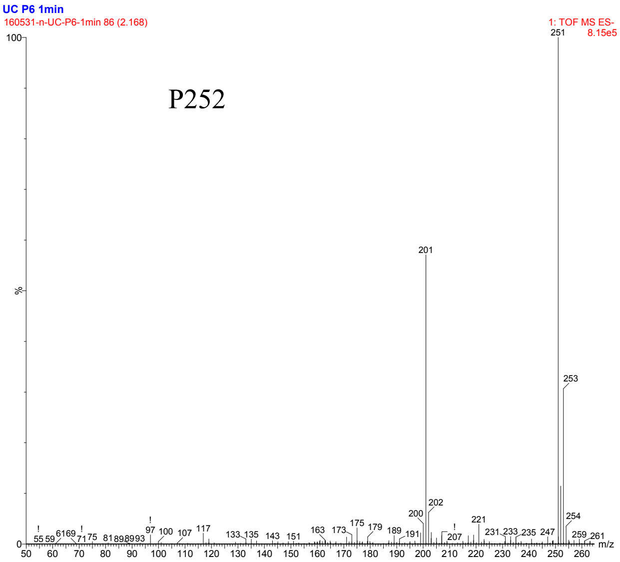
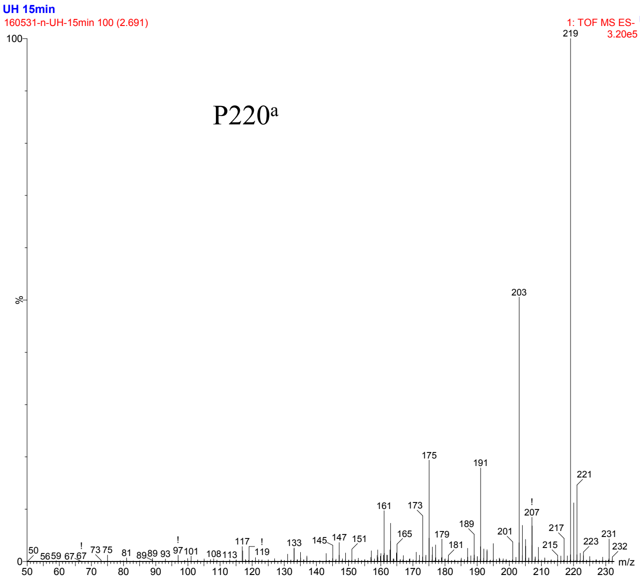
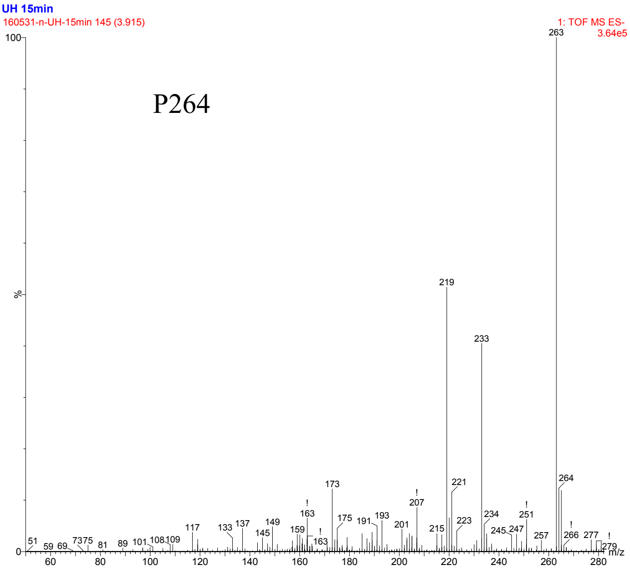


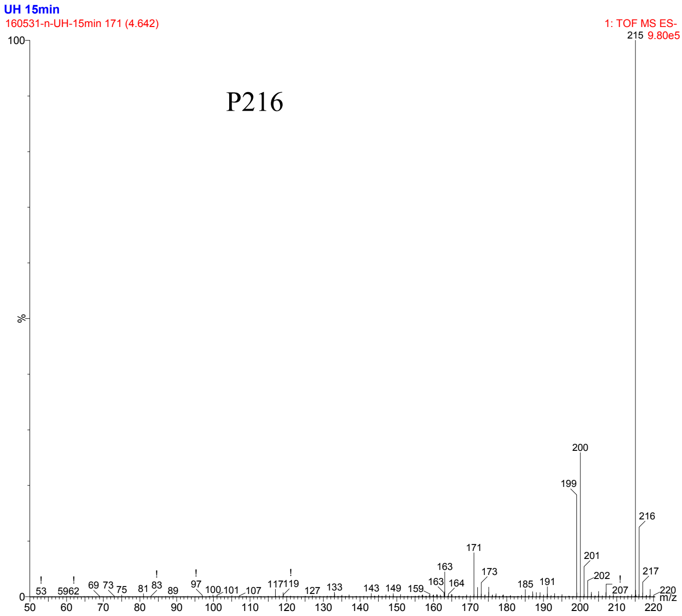
Figure S6. Total ion chromatogram (TIC) under ESI negative mode.

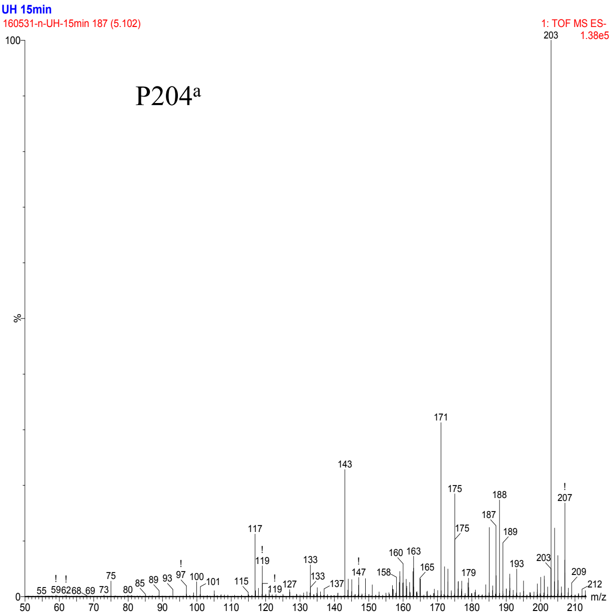

UC P6 3min
160531-n-UC-P6-3min 65 (1.865)
1: TOF MS ES-
1.05e5
P236
235
199
237
221
207
175
151
189
195
205
217
233
247
249
97
117
119
163
173
179
187
%
m/z
100
0

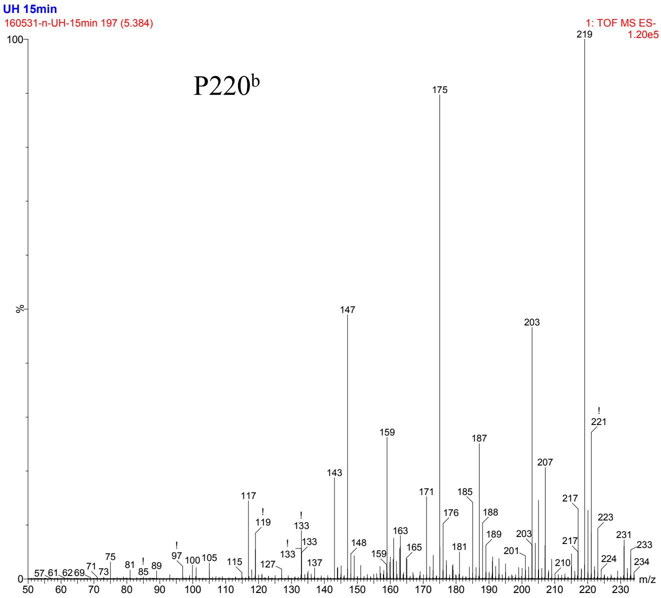

UC P6 1min
160531-n-UC-P6-1min 86 (2.168)
1: TOF MS ES-
8.15e5
P252
251
201
253
202
200
221
254
%
m/z
100
0

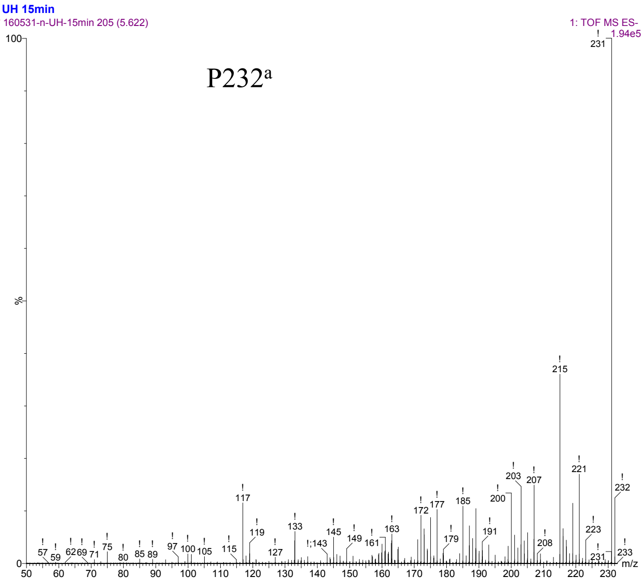

UH 15min
160531-n-UH-15min 100 (2.691)
1: TOF MS ES-
3.20e5
P220a
219
203
175
191
221
161
173
207
189
201
217
231
%
m/z
100
0

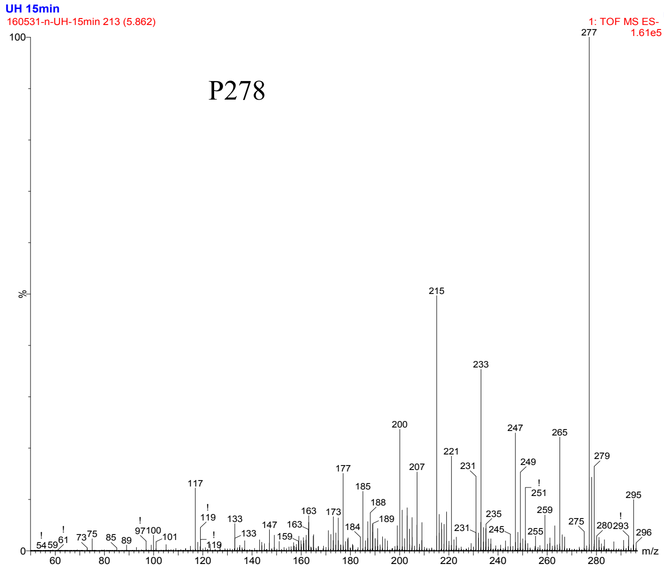

UH 15min
160531-n-UH-15min 145 (3.915)
1: TOF MS ES-
3.64e5
P264
263
219
233
173
221
264
207
163
251
234
%
m/z
100
0


UH 15min
160531-n-UH-15min 171 (4.642)
1: TOF MS ES-
215
9.80e5
P216
200
199
216
171
173
163
201
202
217
%
m/z
100
0


UH 15min
160531-n-UH-15min 187 (5.102)
1: TOF MS ES-
1.38e5
P204a
203
171
143
175
188
187
207
189
117
160
163
%
m/z
100
0


UH 15min
160531-n-UH-15min 197 (5.384)
1: TOF MS ES-
1.20e5
P220b
100
%
0
219
175
147
203
221
159
187
143
207
117
171
185
176
217
188
223
119
133
148
203
189
231
163
181
201
233
165
159
217
75
71
73
81
85
89
97
100
105
115
127
133
137
224
234
57
61
62
69
210
m/z


UH 15min
160531-n-UH-15min 205 (5.622)
1: TOF MS ES-
1.94e5
P232a
100
%
0
231
215
221
203
207
232
200
185
117
172
177
223
133
145
163
119
149
161
179
191
208
231
233
143
127
115
105
100
97
85
89
80
75
71
69
62
59
57
m/z


UH 15min
160531-n-UH-15min 213 (5.862)
1: TOF MS ES-
1.61e5
P278
100
%
0
277
215
233
200
247
265
221
279
177
207
231
249
185
251
295
117
188
163
173
235
259
119
189
275
280
293
133
147
163
184
231
245
255
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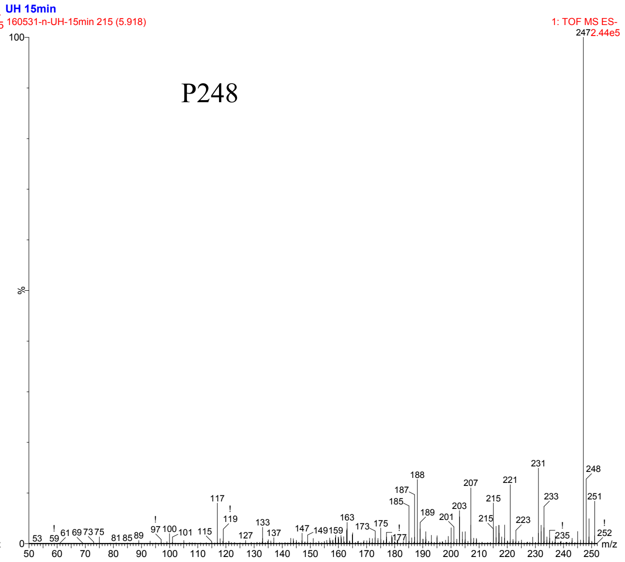
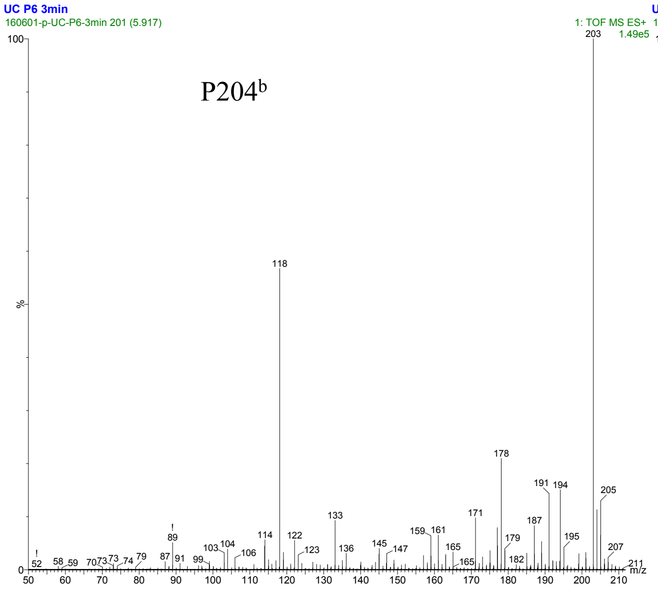
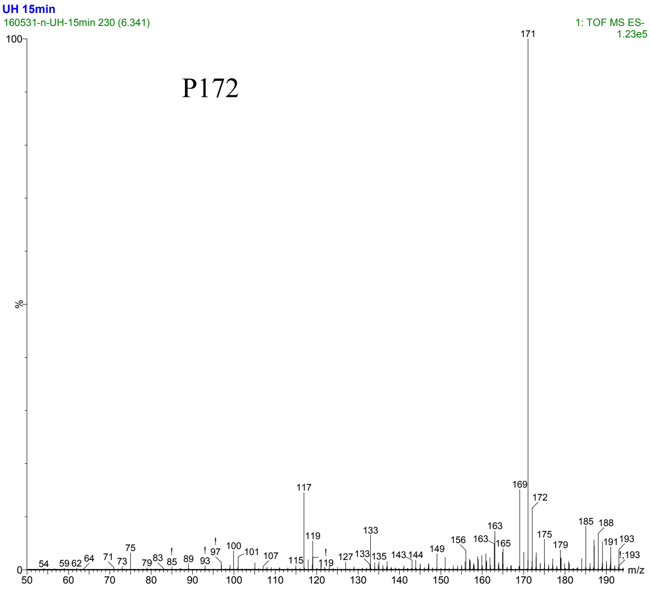
61
73
75
85
89
m/z


UH 15min
160531-n-UH-15min 215 (5.918)
1: TOF MS ES-
247
2.44e5
P248
100
%
0
231
248
188
187
207
221
185
117
233
251
189
203
215
119
133
163
201
215
223
147
149
159
173
175
177
235
252
127
137
97
100
101
115
53
59
61
69
73
75
81
85
89
m/z


UC P6 3min
160601-p-UC-P6-3min 201 (5.917)
1: TOF MS ES+
1.49e5
P204b
100
%
0
203
118
178
191
194
205
133
171
187
89
114
122
159
161
179
195
207
103
104
136
145
123
106
147
165
182
211
87
91
99
52
58
59
70
73
73
74
79
m/z


UH 15min
160531-n-UH-15min 230 (6.341)
1: TOF MS ES-
1.23e5
P172
100
%
0
171
117
169
172
133
185
188
163
175
119
156
163
165
179
191
193
75
100
101
149
97
127
133
135
143
144
193
107
115
119
54
59
62
64
71
73
79
83
85
89
93
m/z

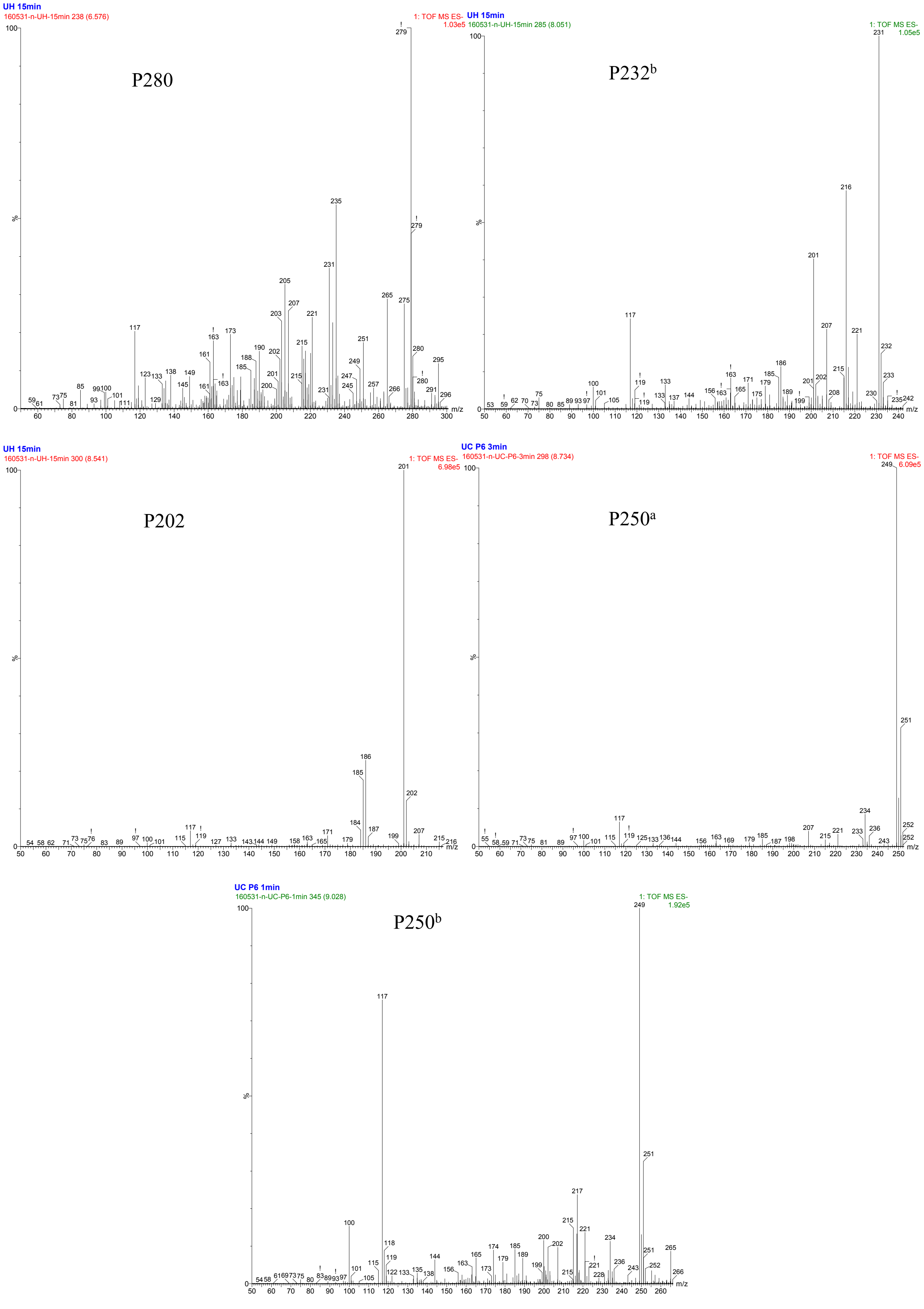


Figure S7. MS and MS2 spectra of the degradation products of NPX by the UV/chlorine and UV/H_2O_2 AOPs under ESI negative mode.

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