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Supplementary material

Degradation of UV filters 2-ethylhexyl-4-methoxycinnamate and 4-*tert*-butyl-4′-methoxydibenzoylmethane in chlorinated water

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First study: effect of pH, temperature, chlorine concentration on the chemical transformation of EHMC and BDM

Tables S1 and S2 present the ANOVA results for the first study about the effects of pH, temperature and chlorine concentration, with their quadratic terms and interactions, on the EHMC and BDM transformation percentage.

Analysing Tables S1 and S2 it is possible to conclude that the models for both UV filters are statistically valid: for a significance level of 5% ($\alpha = 0.05$) the theoretical *F*-value of the model is 2.494, and both the experimental *F*-values of EHMC and BDM are higher (2.955 and 3.647 for EHMC and BDM) and both *P*-values of EHMC and BDM (0.0260 and 0.0105) are lower than the referred significance level.

Regarding the three factors under analysis only pH and temperature seem to have a significant effect on the chemical transformation of EHMC (Table S1): for a significance level of 5% ($\alpha = 0.05$), only the pH and temperature demonstrate higher *F*-values (7.446 and 5.832) than the theoretical value (4.451); in the same trend, both the *P*-values of pH and temperature (0.0143 and 0.0273) are below the significance level of 5%. Also, there is no significant second order or interactions among the three factors. For BDM (Table S2) the chlorine concentration seems to be the only factor with an influence on its transformation with pH being in the threshold: only chlorine demonstrated an *F*-value (13.221) higher than the theoretical value (4.451) and a *P*-value (0.020) lower than the referred significance level.

Second study: study of the effect of pH, temperature, chlorine concentration and DOM on the chemical transformation of EHMC and BDM

Tables S3 and S4 present the ANOVA results for the second study with the inclusion of DOM as a new experimental variable.

From the analysis of Tables S3 and S4 it is possible to conclude that the EHMC model is valid (*F*-value = 16.705) whereas the significance of the calculated model for BDM cannot be concluded because the *F*-value (1.994) is somewhat smaller that the theoretical *F*-value – for a significance level of 5% ($\alpha = 0.05$) the theoretical *F*-value of the model is 2.637. This result may be due to the complexity of the model of BDM as there are a relatively high number of experimental factors under analysis and also maybe due to the chemistry of this UV filter.

For EHMC (Table S3) the temperature seems to be the only factor that influences its chemical transformation more prominently: for a significance level of 5% ($\alpha = 0.05$) the *F* values of pH (*F*-value = 0.07301), chlorine concentration (*F*-value = 0.203) and DOM (*F*-value = 0.06060) are significantly lower than the theoretical number (4.747). On the other hand, temperature demonstrated an *F*-value (196.231) significantly higher than the theoretical one (4.747); in the same trend the *P*-values of pH (0.7916), chlorine (0.6605) and DOM (0.8097) were all slightly above the significance level of 5% with only temperature demonstrating a *P*-value (0.0000) below the referred significance level. The analysis of the effects of second order and interactions shows that the interaction between pH and DOM is significant (*F*-value = 19.906) as well as the pH and chlorine second order terms (*F*-values = 10.102 and 5.923).

For BDM (Table S4) only chlorine and DOM concentrations seem to have a significant effect on its chemical transformation: for a significance level of 5% ($\alpha = 0.05$) only chlorine and DOM concentrations demonstrate higher *F*-values (8.924 and 7.218) than the theoretical one (4.747); in the same trend the *P*-values of chlorine and DOM (0.0113 and 0.0198) are below the significance level of 5%. Also, there is no significant second order effect or interactions among the four factors.

Third study: study of the effect of pH, chlorine concentration, DOM and artificial sunlight irradiation on the chemical transformation of EHMC and BDM

Tables S5 and S6 present the ANOVA results for the third study four factors, pH, chlorine concentration, DOM and artificial sunlight irradiation, keeping temperature constant [average room temperatures (±standard deviation) of 21.3 ºC (±0.7) for EHMC and of 23.0 ºC (±0.7) for BDM].

From the analysis of Tables S5 and S6 it is possible to conclude that the BDM model is valid (*F*-value = 3.532) whereas the significance of the calculated model for EHMC cannot be concluded because the *F*-value (1.442) is somewhat smaller that the theoretical *F*-value – for a significance level of 5% ($\alpha = 0.05$) the theoretical *F*-value of the model is 2.637.

For EHMC the artificial sunlight irradiation seems to be the only significant factor in the chemical transformation of the UV filter with an *F*-value (5.751) higher than the theoretical one (4.747). The analysis of the second order terms and interactions shows that only the factor (pH *v.* Cl) is significant (*F*-value = 5.520).

For BDM the pH (*F*-value = 13.534) and chlorine concentration (*F*-value = 5.447) are the only significant independent factors to the chemical transformation of the UV filter. Regarding second order factors the (pH *v.* pH) (with *F*-value = 18.335) and (Irrad. time *v.* Irrad. time) (with *F*-value = 10.550) are also significant to the chemical transformation of BDM. Another important interaction seems to be (DOM *v.* Irrad. time) (with *F*-value = 4.799).

Table S1. ANOVA for the analysis of the effects on the EHMC chemical transformation response surface obtained using a Box Behnken design

SS, sum of squares; d.f., degrees of freedom; MS, mean squares; *F*, Fisher ratio; *P*, probability of getting the *F*-ratio under the null hypothesis; β, regression coefficient from a multiple linear regression analysis; SE_β, standard error of β

Variable	SS	d.f.	MS	*F*	*P*	β	SE_β
Summary							
Model	5264	9	584.932	2.955	0.0260		
Error	3365	17	197.938				
Adjusted total	8629	26	331.897				
Factor							
Intercept	6395	1	6395	32.308	0.0000	46.170	8.123
pH	1474	1	1474	7.446	0.0143	–3.199	1.172
T	1154	1	1154	5.832	0.0273	0.849	0.352
Cl	773.118	1	773.118	3.906	0.0646	–6.951	3.517
pH × *T*	117.735	1	117.735	0.595	0.4512	2.361	3.061
pH × Cl	378.262	1	378.262	1.911	0.1847	4.232	3.061
T × Cl	0.0595	1	0.0595	0.0003	0.9864	–0.053	3.061
pH × pH	914.134	1	914.134	4.618	0.0463	7.830	3.643
T × *T*	38.856	1	38.856	0.196	0.6633	1.614	3.643
Cl × Cl	128.857	1	128.857	0.651	0.4309	–2.940	3.643
Model check							
Main	3401	3	1134				
Int	496.057	3	165.352	0.835	0.4929		
Int + Squ	1367	3	455.706	2.302	0.1137		
Squ	1367	3	455.706	2.302	0.1137		
Error	3365	17	197.938				
Lack of fit							
Lack of Fit	1357	3	452.181	3.152	0.0585		
Pure Error	2008	14	143.457				
Total Error	3365	17	197.938				

Table S2. ANOVA for the analysis of the effects on the BDM chemical transformation response surface obtained using a Box Behnken design

SS, sum of squares; d.f., degrees of freedom; MS, mean squares; *F*, Fisher ratio; *P*, probability of getting the *F*-ratio under the null hypothesis; β, regression coefficient from a multiple linear regression analysis; SE_{β}, standard error of β

Variable	SS	d.f.	MS	*F*	*P*	β	SE_{β}
Summary							
Model	2234	9	248.275	3.647	0.0105		
Error	1157	17	68.084				
Adjusted total	3392	26	130.458				
Factor							
Intercept	22090	1	22090	324.478	0.0000	85.813	4.764
pH	283.333	1	283.333	4.162	0.0572	1.403	0.688
T	0.009	1	0.009	0.0001	0.9910	–0.002	0.206
Cl	900.148	1	900.148	13.221	0.0020	50.004	13.752
pH × *T*	10.905	1	10.905	0.160	0.6940	0.718	1.795
pH × Cl	108.561	1	108.561	1.595	0.2237	–2.267	1.795
T × Cl	47.142	1	47.142	0.692	0.4169	1.494	1.795
pH × pH	473.062	1	473.062	6.948	0.0173	5.632	2.137
T × *T*	64.842	1	64.842	0.952	0.3428	–2.085	2.137
Cl × Cl	89.668	1	89.668	1.317	0.2670	–2.452	2.137
Model check							
Main	1183	3	394.497				
Int	166.607	3	55.536	0.816	0.5028		
Int + Squ	884.372	3	294.791	4.330	0.0193		
Squ	884.372	3	294.791	4.330	0.0193		
Error	1157	17	68.084				
Lack of fit							
Lack of Fit	353.181	3	117.760	2.050	0.1531		
Pure Error	804.150	14	57.439				
Total Error	1157	17	68.084				

Table S3. ANOVA for the analysis of the effects on the EHMC chemical transformation response obtained using a Box Behnken design

SS, sum of squares; d.f., degrees of freedom; MS, mean squares; *F*, Fisher ratio; *P*, probability of getting the *F*-ratio under the null hypothesis; β, regression coefficient from a multiple linear regression analysis; SE_β, standard error of β

Variable	SS	d.f.	MS	*F*	*P*	β	SE_β
Summary							
Model	5406	14	386.128	16.705	0.0000		
Error	277.372	12	23.114				
Adjusted total	5683	26	218.583				
Factor							
Intercept	3287	1	3287	142.199	0.0000	33.100	2.776
pH (A)	1.688	1	1.688	0.073	0.7916	–0.125	0.463
T (B)	4536	1	4536	196.231	0.0000	1.944	0.139
Cl (C)	4.687	1	4.687	0.203	0.6605	0.625	1.388
DOM (D)	1.401	1	1.401	0.0606	0.8097	0.06840	0.278
pH × *T*	1.562	1	1.562	0.0676	0.7993	0.288	1.109
pH × Cl	8.703	1	8.703	0.376	0.5509	–0.681	1.109
pH × DOM	460.102	1	460.102	19.906	0.0008	–4.950	1.109
T × Cl	16.810	1	16.810	0.727	0.4105	–0.946	1.109
T × DOM	25.000	1	25.000	1.082	0.3188	1.154	1.109
Cl × DOM	10.890	1	10.890	0.471	0.5055	–0.762	1.109
pH × pH	233.496	1	233.496	10.102	0.0079	3.054	0.961
T × *T*	0.926	1	0.926	0.040	0.8447	0.192	0.961
Cl × Cl	136.913	1	136.913	5.923	0.0315	2.338	0.961
DOM × DOM	84.978	1	84.978	3.676	0.0793	1.842	0.961
Model check							
Main	4544	4	1136				
Int	523.068	6	87.178	3.772	0.0240		
Int + Squ	339.212	4	84.803	3.669	0.0356		
Squ	339.212	4	84.803	3.669	0.0356		
Error	277.372	12	23.114				
Lack of fit							
Lack of Fit	230.252	10	23.025	0.977	0.6058		
Pure Error	47.120	2	23.560				
Total Error	277.372	12	23.114				

Table S4. ANOVA for the analysis of the effects on the BDM chemical transformation response obtained using a Box Behnken design

SS, sum of squares; d.f., degrees of freedom; MS, mean squares; *F*, Fisher ratio; *P*, probability of getting the *F*-ratio under the null hypothesis; β, regression coefficient from a multiple linear regression analysis; SE_β, standard error of β

Variable	SS	d.f.	MS	*F*	*P*	β	SE_β
Summary							
Model	1486	14	106.163	1.994	0.1188		
Error	638.782	12	53.232				
Adjusted total	2125	26	81.733				
Factor							
Intercept	997.364	1	997.364	18.736	0.0010	18.233	4.212
pH	184.867	1	184.867	3.473	0.0870	1.308	0.702
T	40.701	1	40.701	0.765	0.3991	–0.184	0.211
Cl	475.021	1	475.021	8.924	0.0113	139.815	46.804
DOM	384.201	1	384.201	7.218	0.0198	–1.133	0.422
pH × *T*	73.960	1	73.960	1.389	0.2614	–1.985	1.684
pH × Cl	81.902	1	81.902	1.539	0.2385	2.088	1.684
pH × DOM	0.640	1	0.640	0.0120	0.9145	0.185	1.684
T × Cl	28.622	1	28.622	0.538	0.4775	1.235	1.684
T × DOM	0.640	1	0.640	0.0120	0.9145	–0.185	1.684
Cl × DOM	138.062	1	138.062	2.594	0.1333	–2.712	1.684
pH × pH	13.796	1	13.796	0.259	0.6199	0.742	1.458
T × *T*	26.601	1	26.601	0.500	0.4931	1.031	1.458
Cl × Cl	71.378	1	71.378	1.341	0.2694	1.688	1.458
DOM × DOM	12.134	1	12.134	0.228	0.6416	0.696	1.458
Model check							
Main	1085	4	271.198				
Int	323.828	6	53.971	1.014	0.4607		
Int + Squ	77.664	4	19.416	0.365	0.8291		
Squ	77.664	4	19.416	0.365	0.8291		
Error	638.782	12	53.232				
Lack of fit							
Lack of Fit	637.075	10	63.707	74.657	0.0133		
Pure Error	1.707	2	0.853				
Total Error	638.782	12	53.232				

Table S5. ANOVA for the analysis of the effects on the EHMC chemical transformation response obtained using a Box Behnken design

SS, sum of squares; d.f., degrees of freedom; MS, mean squares; *F*, Fisher ratio; *P*, probability of getting the *F*-ratio under the null hypothesis; β, regression coefficient from a multiple linear regression analysis; SE_{β}, standard error of β

Variable	SS	d.f.	MS	*F*-ratio	*P*	β	SE_{β}
Summary							
Model	5253	14	375.234	1.442	0.2655		
Error	3122	12	260.200				
Adjusted total	8376	26	322.141				
Factor							
Intercept	3066	1	3066	11.782	0.0060	31.967	9.313
pH (A)	1.613	1	1.613	0.006	0.9385	0.122	1.552
Cl (B)	209.168	1	209.168	0.804	0.3876	–4.175	4.657
DOM (C)	224.467	1	224.467	0.863	0.3713	–0.866	0.932
Irrad. time (D)	1496	1	1496	5.751	0.0336	–0.744	0.310
pH × Cl	1436	1	1436	5.520	0.0367	–8.746	3.722
pH × DOM	171.610	1	171.610	0.660	0.4325	3.023	3.722
pH × Irrad. time	0.160	1	0.160	0.0006	0.9806	–0.09231	3.722
Cl × DOM	492.840	1	492.840	1.894	0.1939	5.123	3.722
Cl × Irrad. time	7.563	1	7.563	0.029	0.8675	0.635	3.722
DOM × Irrad. time	36.602	1	36.602	0.141	0.7142	1.396	3.722
pH × pH	603.974	1	603.974	2.321	0.1535	4.912	3.224
Cl × Cl	32.122	1	32.122	0.123	0.7314	1.133	3.224
DOM × DOM	308.391	1	308.391	1.185	0.2977	3.510	3.224
Irrad. time × Irrad. time	86.761	1	86.761	0.333	0.5743	–1.862	3.224
Model check							
Main	1932	4	482.896				
Int	2145	6	357.531	1.374	0.3004		
Int + Squ	1177	4	294.126	1.130	0.3879		
Squ	1177	4	294.126	1.130	0.3879		
Error	3122	12	260.200				
Lack of fit							
Lack of Fit	3091	10	309.060	19.434	0.0499		
Pure Error	31.807	2	16.903				
Total Error	3122	12	260.200				

Table S6. ANOVA for the analysis of the effects on the BDM chemical transformation response obtained using a Box Behnken design

SS, sum of squares; d.f., degrees of freedom; MS, mean squares; *F*, Fisher ratio; *P*, probability of getting the *F*-ratio under the null hypothesis; β, regression coefficient from a multiple linear regression analysis; SE_β, standard error of β

Variable	SS	d.f.	MS	*F*-ratio	*P*	β	SE_β
Summary							
Model	6544	14	467.397	3.532	0.0173		
Error	1588	12	132.333				
Adjusted total	8132	26	312.752				
Factor							
Intercept	43.320	1	43.320	0.327	0.5778	3.800	6.642
pH (A)	1791	1	1791	13.534	0.0032	4.072	1.107
Cl (B)	720.753	1	720.753	5.447	0.0378	172.222	73.796
DOM (C)	1.613	1	1.613	0.0122	0.9139	0.07341	0.665
Irrad. time (D)	0.653	1	0.653	0.0049	0.9451	0.02334	0.332
pH × Cl	24.503	1	24.503	0.185	0.6746	1.142	2.655
pH × DOM	60.839	1	60.839	0.460	0.5106	1.800	2.655
pH × Irrad. time	30.802	1	30.802	0.233	0.6382	–1.281	2.655
Cl × DOM	299.291	1	299.291	2.262	0.1585	–3.992	2.655
Cl × Irrad. time	6.502	1	6.502	0.049	0.8283	0.588	2.655
DOM × Irrad. time	635.044	1	635.044	4.799	0.0490	–5.815	2.655
pH × pH	2426	1	2426	18.335	0.0011	9.844	2.299
Cl × Cl	250.559	1	250.559	1.893	0.1940	3.163	2.299
DOM × DOM	302.335	1	302.335	2.285	0.1565	3.475	2.299
Irrad. time × Irrad. time	1396	1	1396	10.550	0.0070	7.467	2.299
Model check							
Main	2514	4	628.495				
Int	1057	6	176.163	1.331	0.3162		
Int + Squ	2973	4	743.152	5.616	0.0088		
Squ	2973	4	743.152	5.616	0.0088		
Error	1588	12	132.333				
Lack of fit							
Lack of Fit	1587	10	158.686	278.396	0.0036		
Pure Error	1.140	2	0.570				
Total Error	1588	12	132.333				

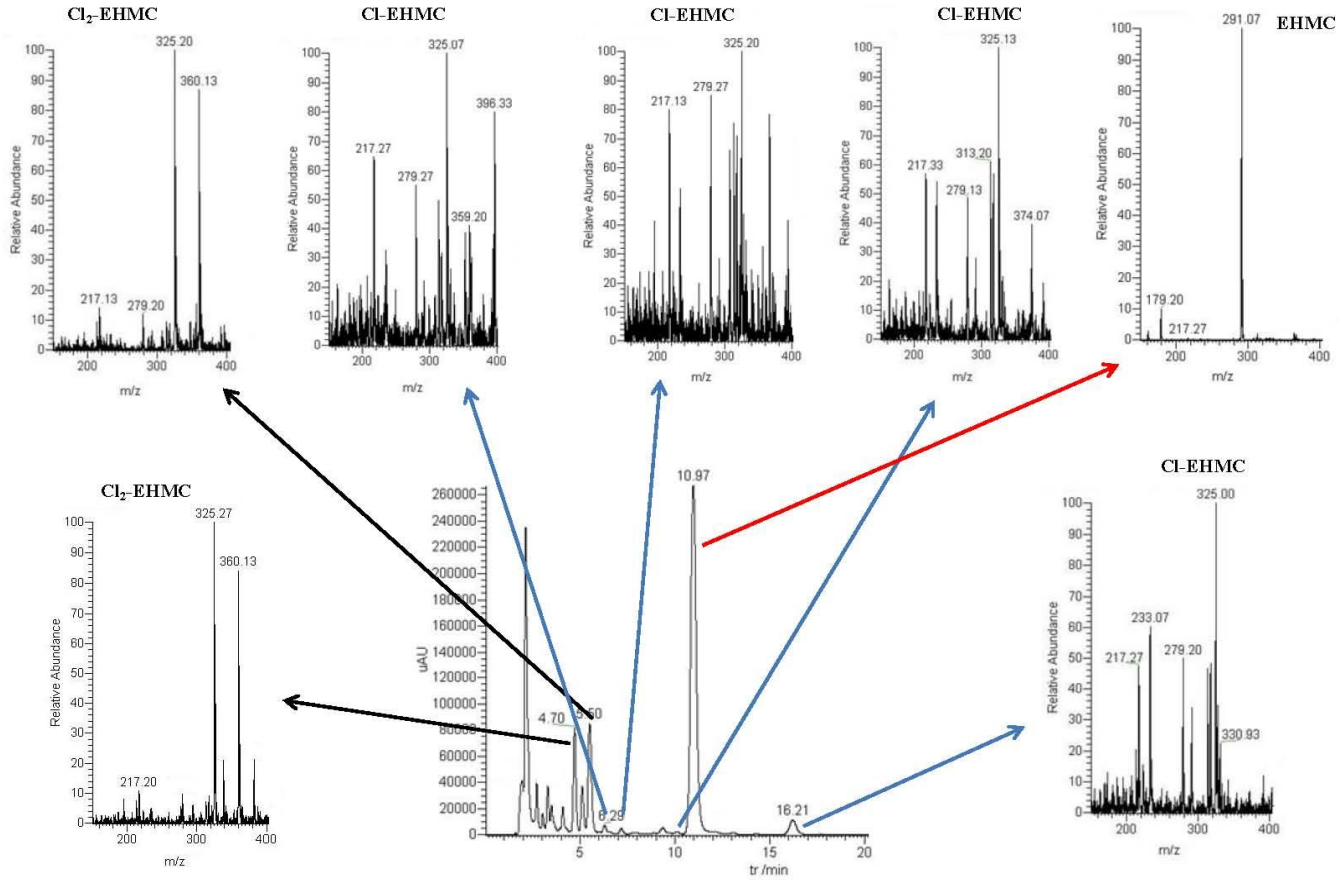

Fig. S1. HPLC chromatogram and MS spectra of the mixture resulting from the reaction of EHMC with chlorine.

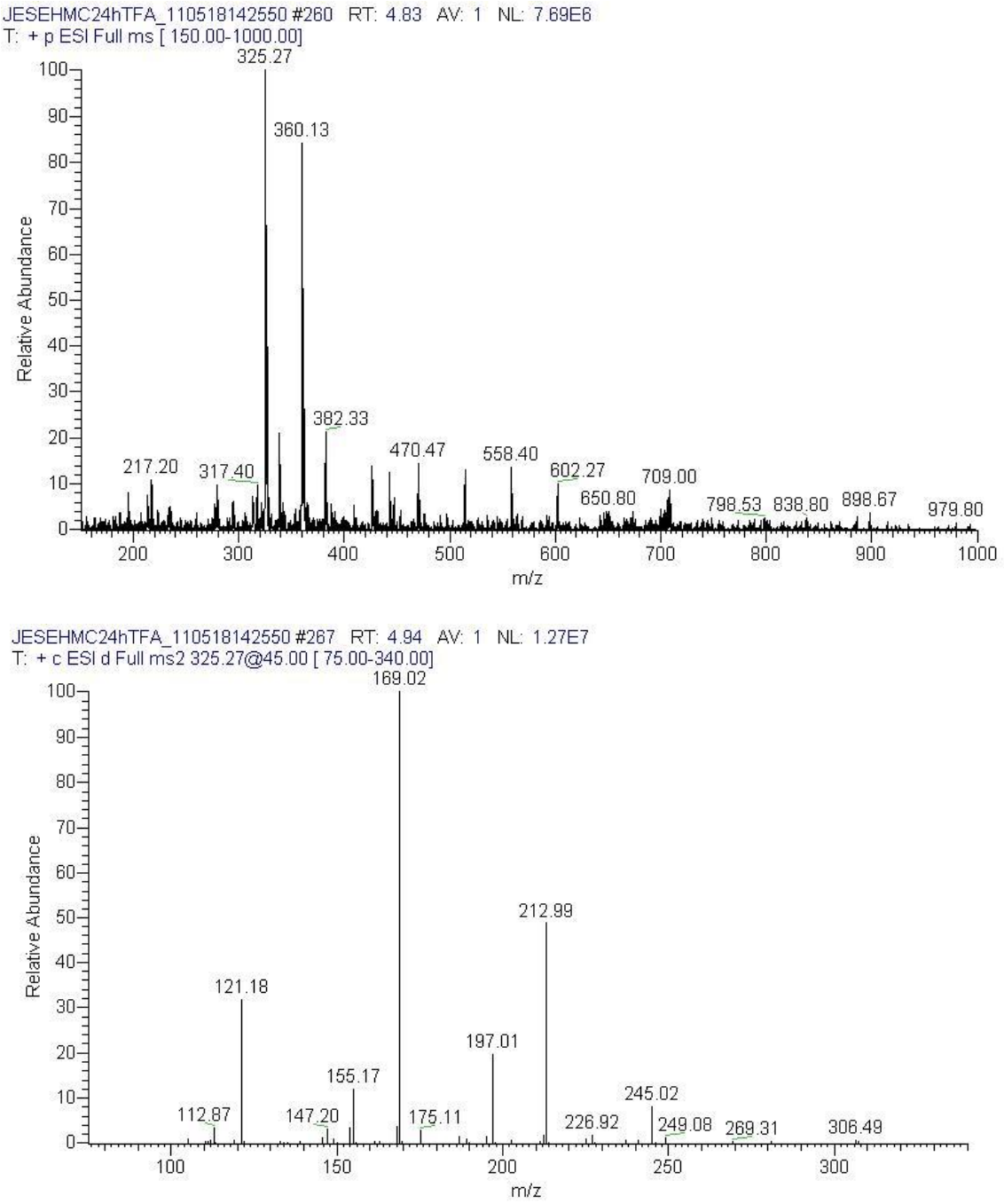

Fig. S2. MS spectra (1st and 2nd fragmentation) for the peak with retention time 4.70 min.

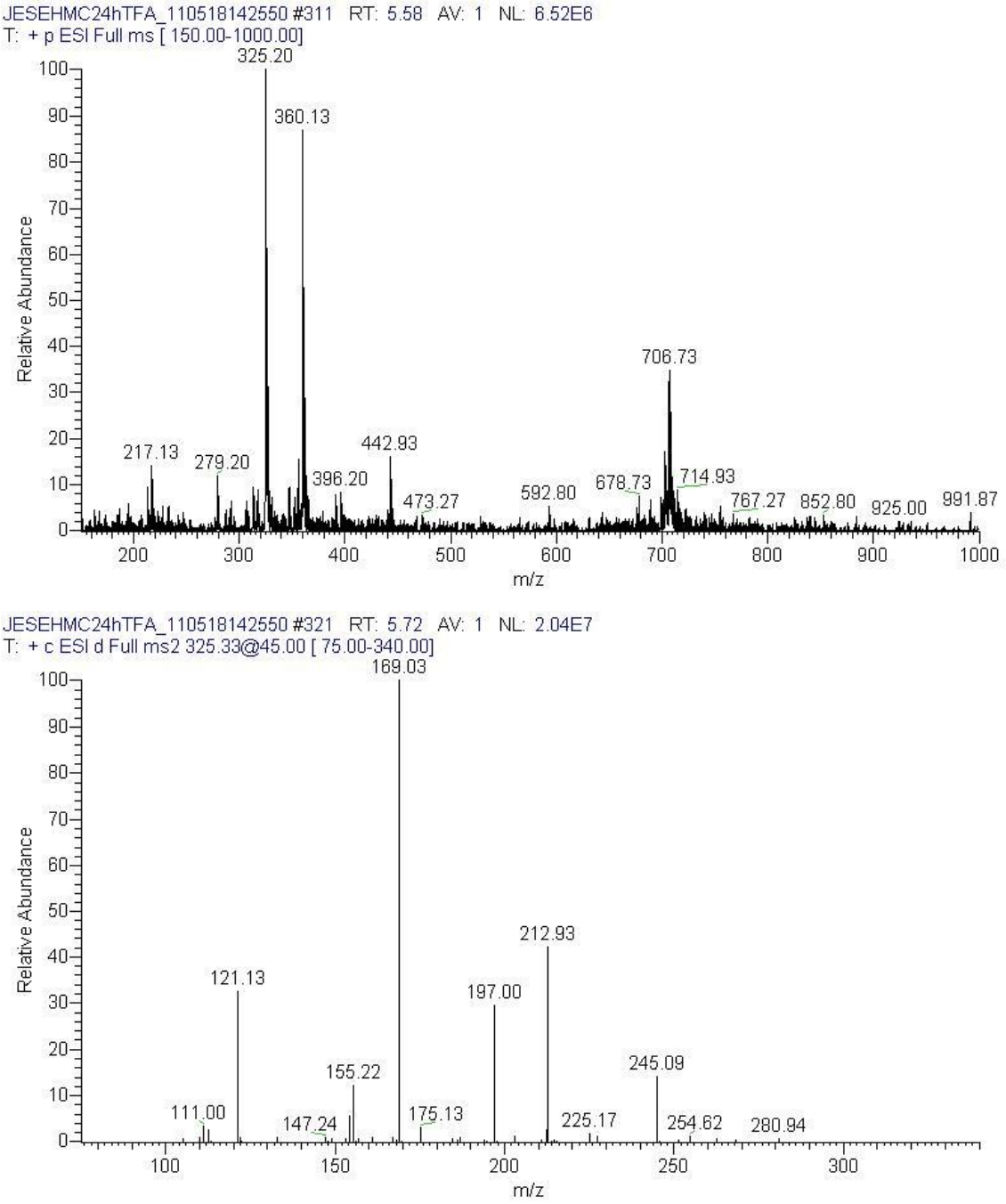

Fig. S3. MS spectra (1st and 2nd fragmentation) for the peak with retention time 5.50 min.

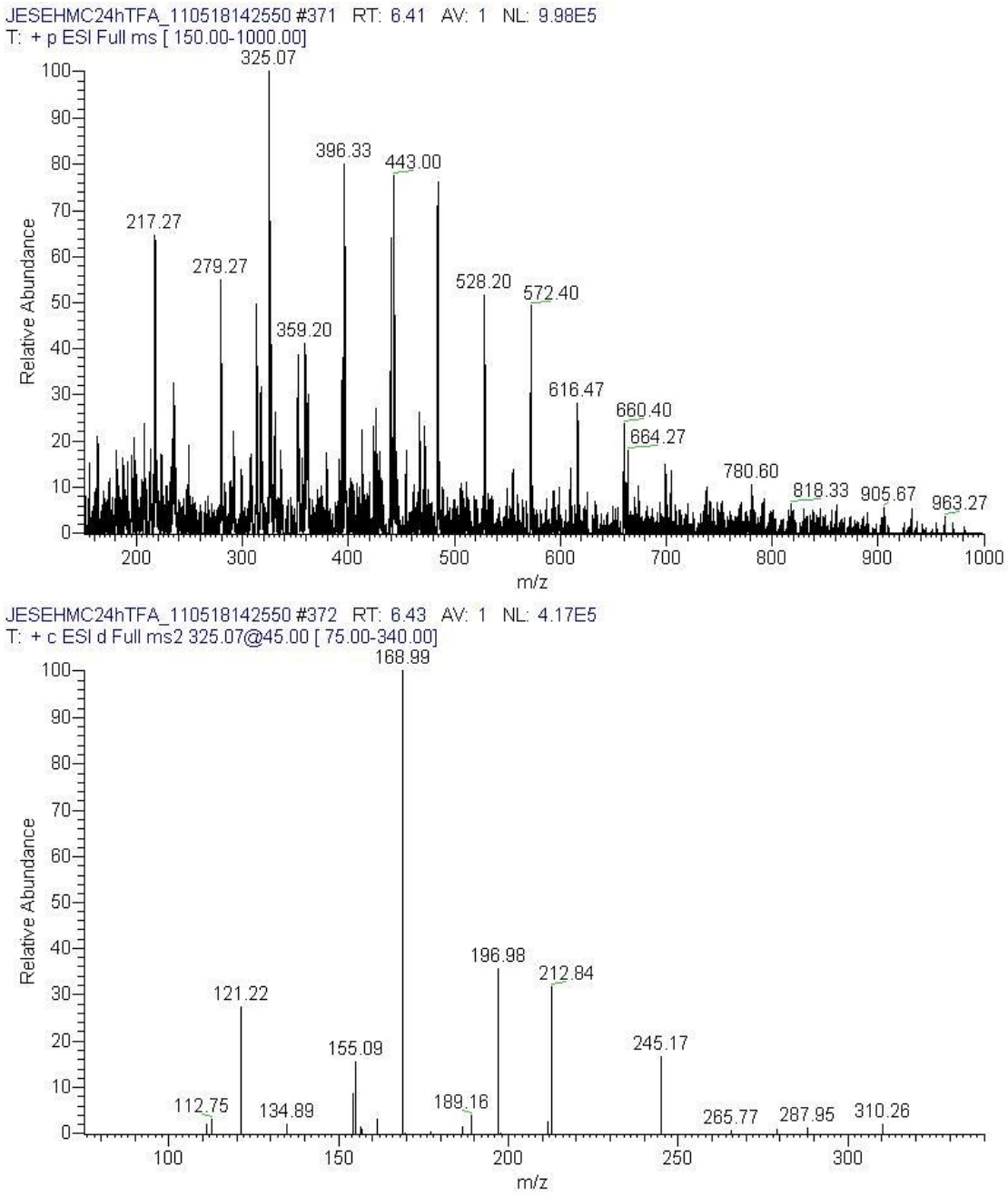

Fig. S4. MS spectra (1st and 2nd fragmentation) for the peak with retention time 6.29 min.

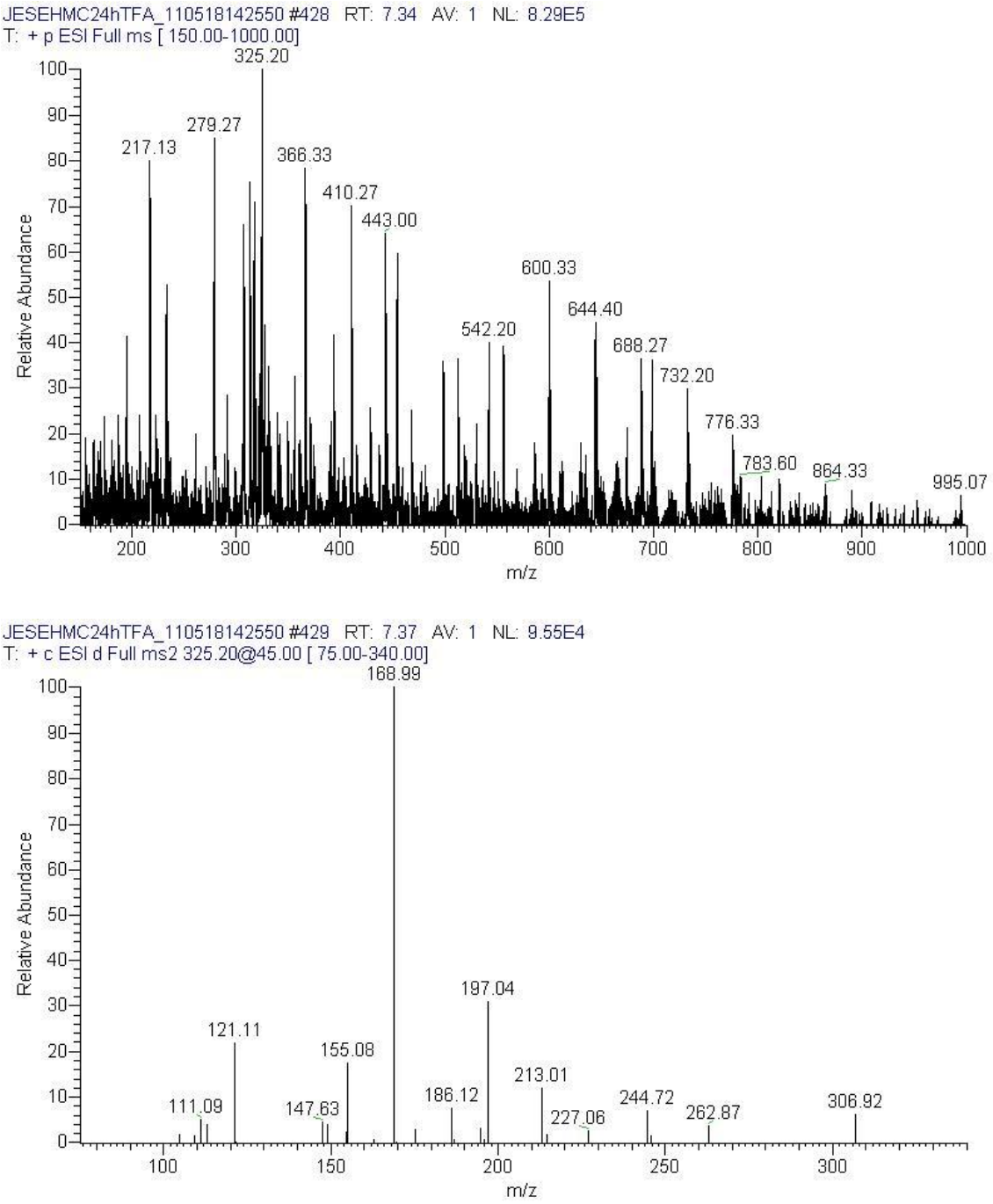

Fig. S5. MS spectra (1st and 2nd fragmentation) for the peak with retention time 7.17 min.

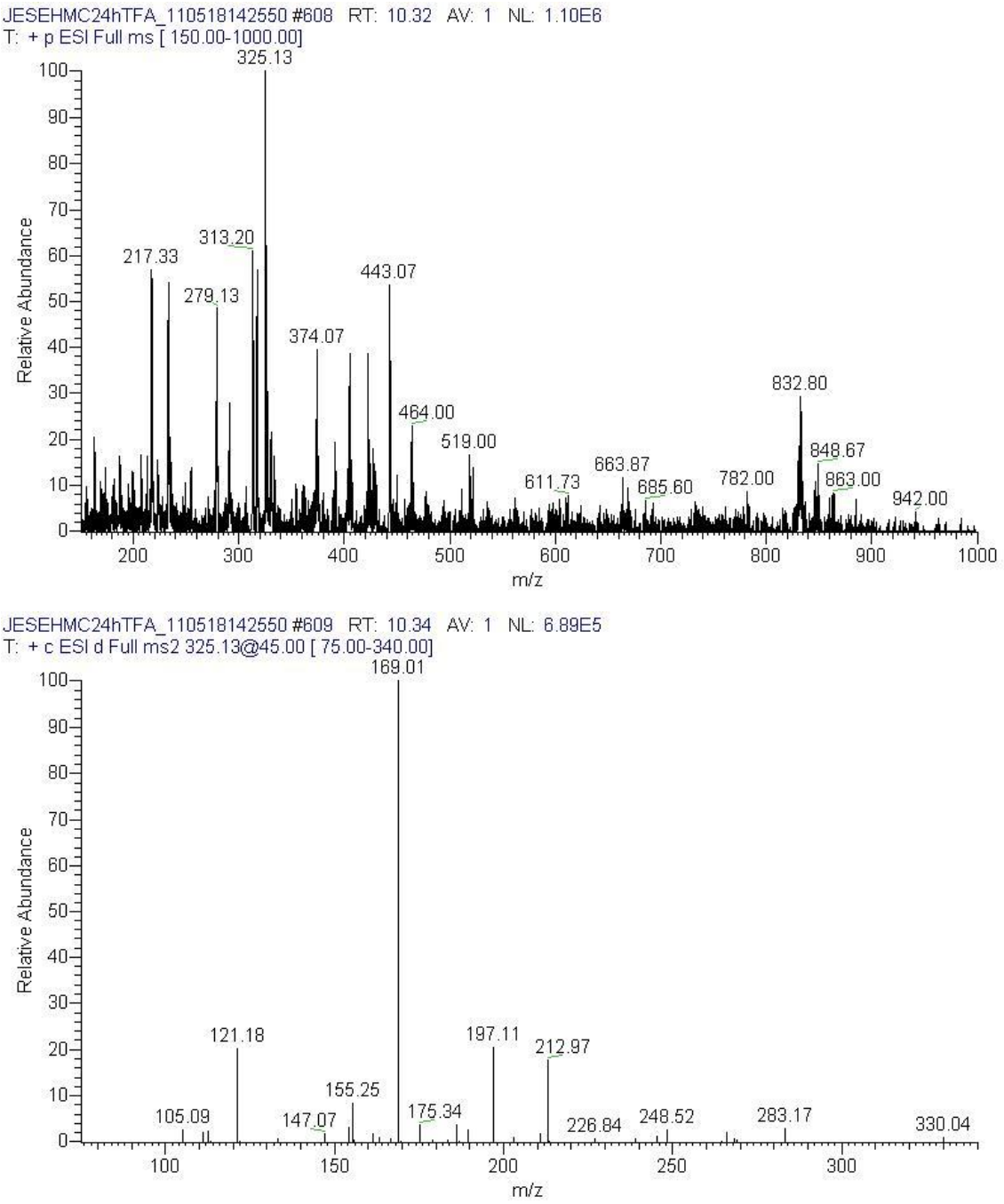

Fig. S6. MS spectra (1st and 2nd fragmentation) for the peak with retention time 10.11 min.

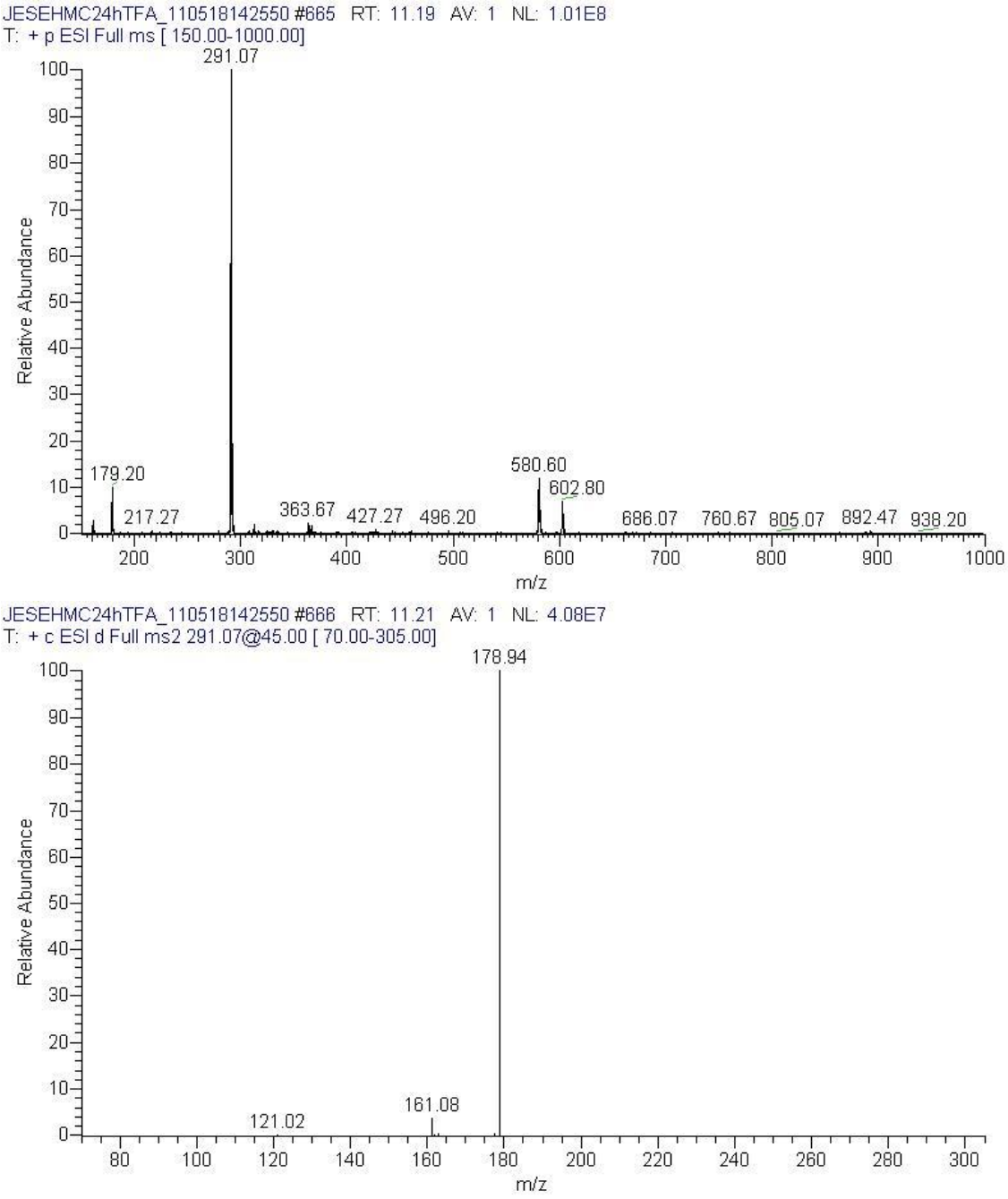

Fig. S7. MS spectra (1st and 2nd fragmentation) for the peak with retention time 10.97 min.

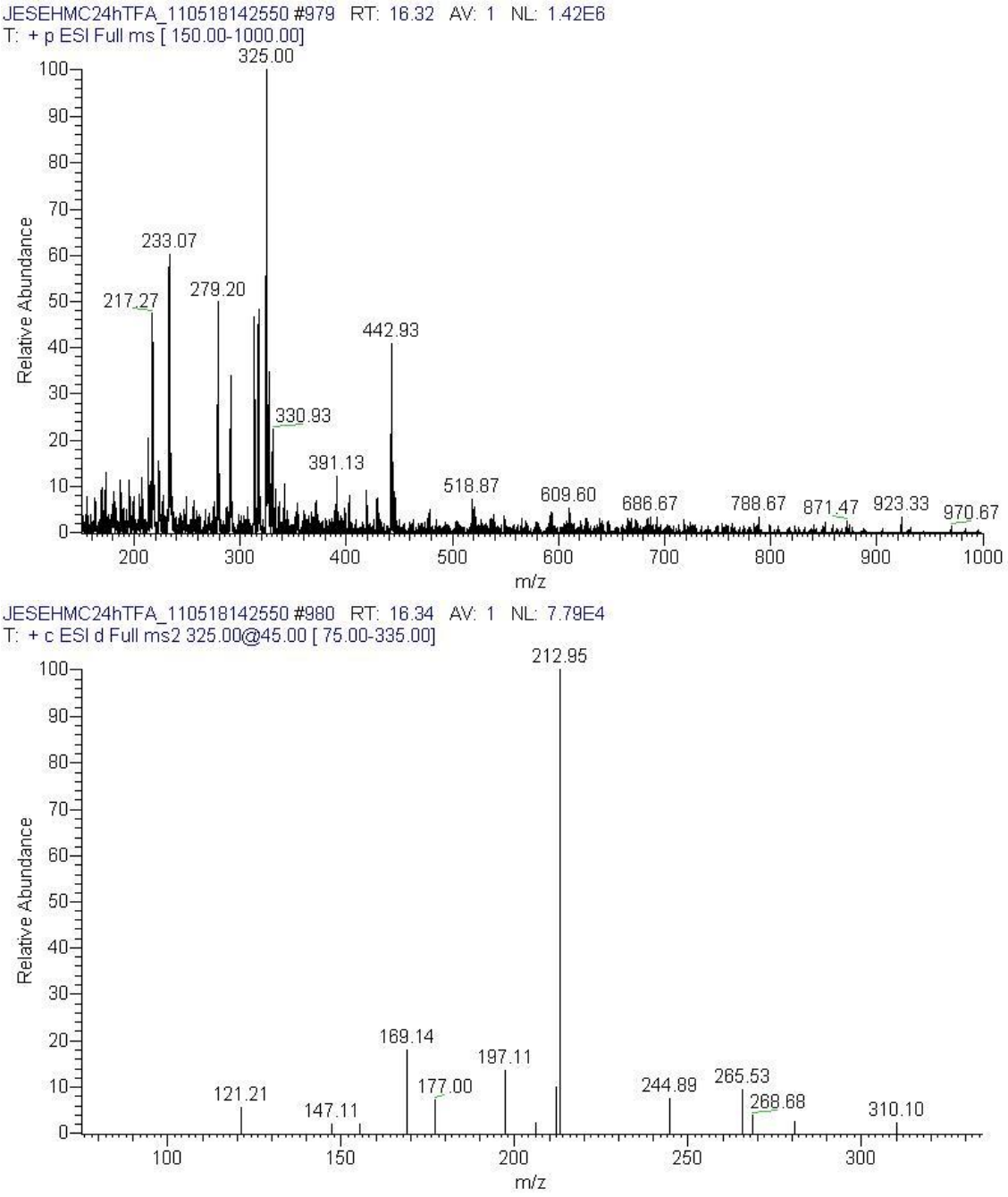

Fig. S8. MS spectra (1st and 2nd fragmentation) for the peak with retention time 16.21 min.

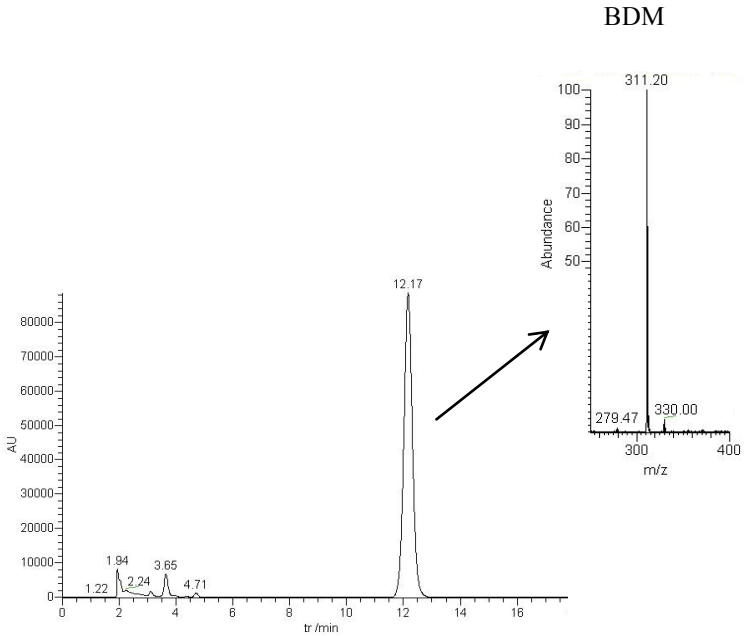

Fig. S9. HPLC chromatogram and MS spectra of BDM (without addition of chlorine).

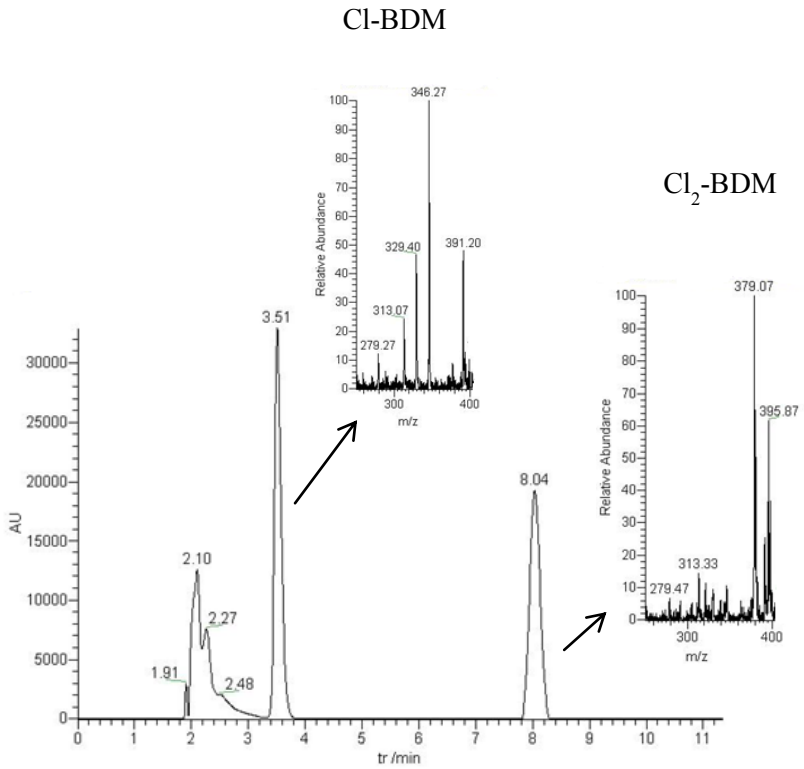

Fig. S10. HPLC chromatogram and MS spectra of the mixture resulting from the reaction of BDM with chlorine.

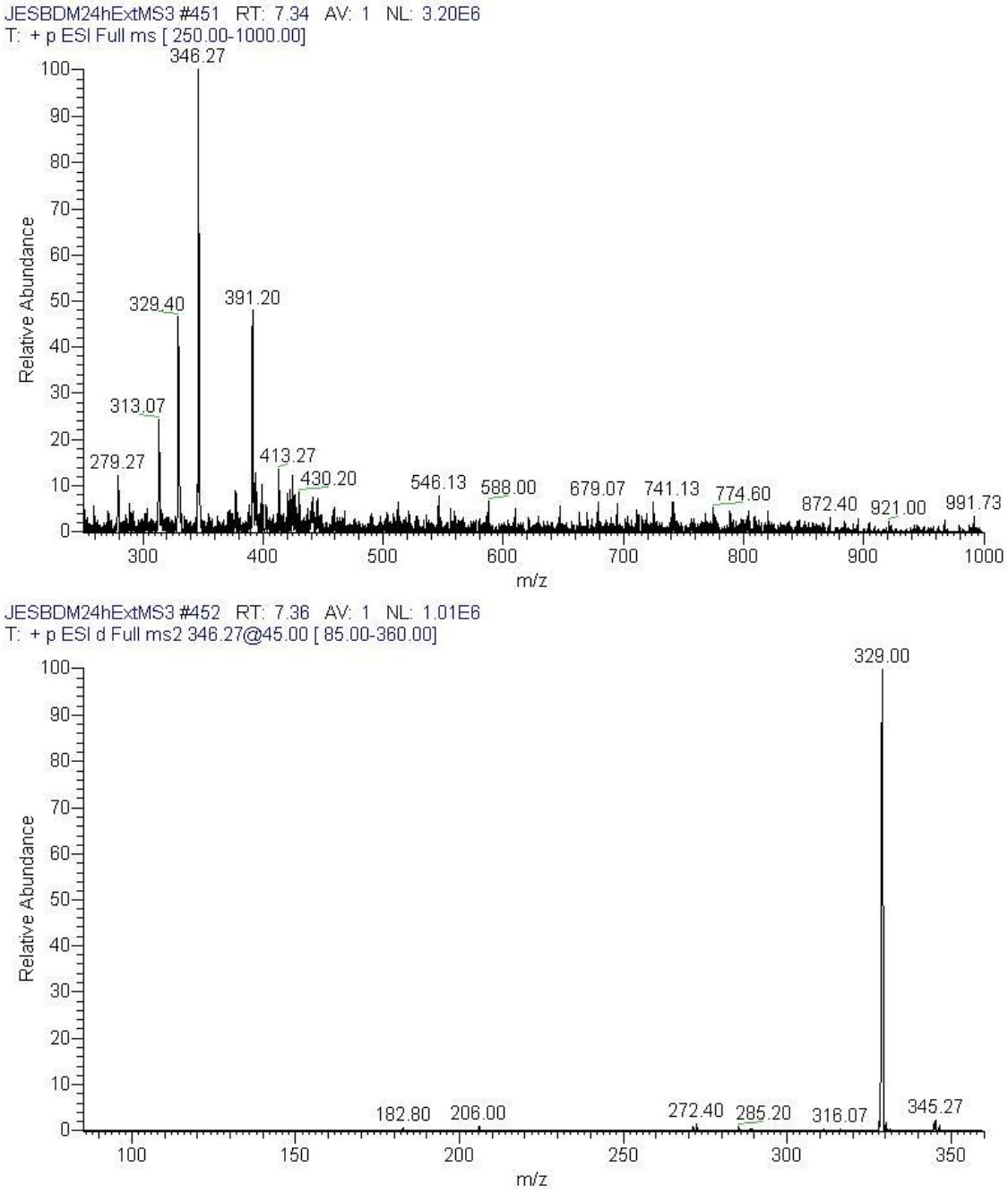

Fig. S11. MS spectra (1st and 2nd fragmentation) for the peak with retention time 3.51 min.

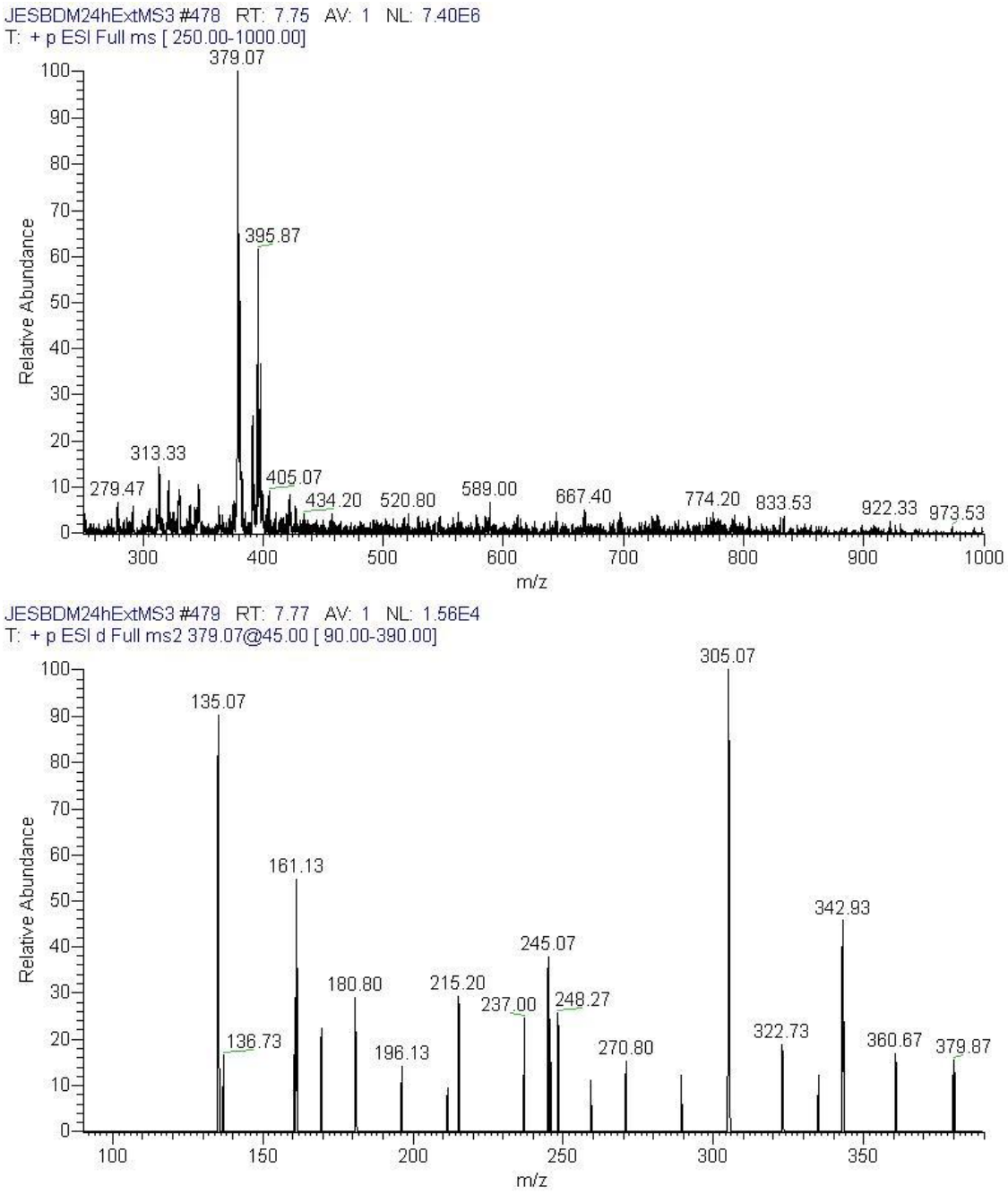

Fig. S12. MS spectra (1st and 2nd fragmentation) for the peak with retention time 8.04 min.