

Supporting Information

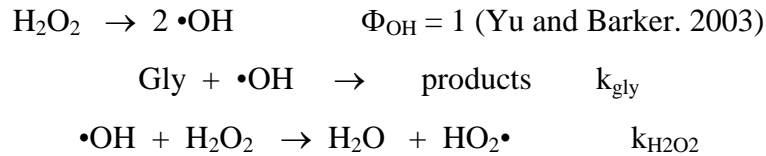
**Effect of UVC pre-irradiation on the Suwannee river natural organic matter (SRNOM)
photooxidant properties: role of carbonyls**

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Text 1 : Measurement of I_0 , the photon flux entering into the solution from the UVC source

I_0 was evaluated by chemical actinometry from the rate of glyphosate consumption in the presence of H_2O_2 in the device. Irradiation of H_2O_2 yields $\bullet OH$ radicals that react with glyphosate according to:



Based on $k_{gly} = 3.7 \times 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$ [Vidal et al. 2015] and $k_{H_2O_2} = 2.7 \times 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$ [Stephan et al. 1996], one gets that glyphosate (10^{-5} M) in presence of H_2O_2 (10^{-5} M) traps 58% of $\bullet OH$ radicals. The rate of glyphosate loss (R_{gly}) is thus equal to :

$$R_{Gly} = I_a^{H_2O_2} \times \Phi_{OH} \times 0.58 = I_0 \times (1 - 10^{-A^{H_2O_2}}) \times \Phi_{OH} \times 0.58$$

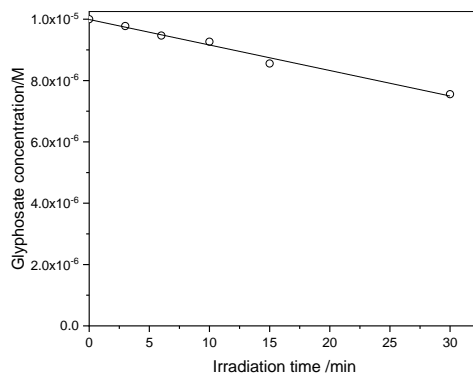
where $I_a^{H_2O_2}$ is the rate of light absorption by H_2O_2 , $A^{H_2O_2}$ is the absorbance of the solution at 254 nm. As only H_2O_2 absorbs 254 nm radiations, one gets :

$$A^{H_2O_2} = \epsilon_{H_2O_2} \times [H_2O_2] \times \ell$$

with $\epsilon_{H_2O_2} = 19.6 \text{ M}^{-1} \cdot \text{cm}^{-1}$, $[H_2O_2] = 10^{-5} \text{ M}$ and $\ell = 2 \text{ cm}$.

From $R_{gly} = (9.3 \pm 0.5) \times 10^{-8} \text{ min}^{-1}$ (Fig SI-1), we get $I_0 = 2.9 \times 10^{-6} \text{ Einstein L}^{-1} \text{ s}^{-1}$

Fig SI-1 : Loss of glyphosate (10^{-5} M) upon irradiation in the presence of H_2O_2 (10^{-5} M) in the UVC device equipped with 4 germicidal tubes (General Electric, 15W).



Vidal E., Negro A., Cassano A., Zalazar C. Simplified reaction kinetics. models and experiments for glyphosate degradation in water by the UV/H₂O₂ process
Photochem Photobiol Sci 2015, 14, 366-377

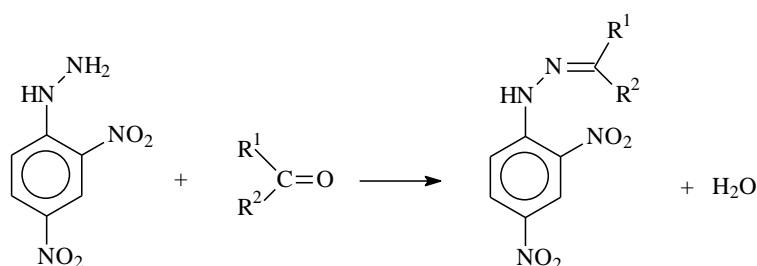
Stefan M. , Hoy A., Bolton J.R. Kinetics and Mechanism of the Degradation and Mineralization of Acetone in Dilute Aqueous Solution Sensitized by the UV Photolysis of Hydrogen Peroxide
Environ. Sci. Technol. 1996, 30, 2382-2390

Yu X.Y., Barker J. R. Hydrogen Peroxide Photolysis in Acidic Aqueous Solutions Containing Chloride Ions. II. Quantum Yield of HO[•](Aq) Radicals J. Phys. Chem. A 2003, 107, 9, 1325–1332

Text 2 : Analysis of carbonyls by DNPH derivatization.

DNPH derivatives were prepared by mixing 1 mL of non irradiated or irradiated SRNOM solution with 200 μ L of DNPH solution (1 mg.mL⁻¹ in acetonitrile) and 20 μ L of phosphoric acid at 5 N. Mixture was mechanically stirred for 30 min. After the addition of 1 mL of acetonitrile, it was shortly analyzed by ultra-high performance liquid chromatography (UHPLC) coupled to high resolution mass spectrometry (HRMS).

In the presence of DNPH carbonyls yield imines and water according to:



The m/z value of the imine is used to determine the chemical formula of the carbonyl. Pyruvic acid (C₃H₄O₃) gives an adduct detected at m/z = 267.0374 in negative mode corresponding to C₉H₇O₆N₄. Methyl glyoxal (C₃H₄O₂) that contains 2 carbonyls is derivatized 2 times and gives an adduct detected at m/z = 431.0709 corresponding to C₁₅H₁₁O₈N₈.

Pyruvic acid and methylglyoxal were used as references for peak quantification for mono and dicarbonyls, respectively.

Fig SI-2 : Calibration curve of pyruvic acid and methylglyoxal

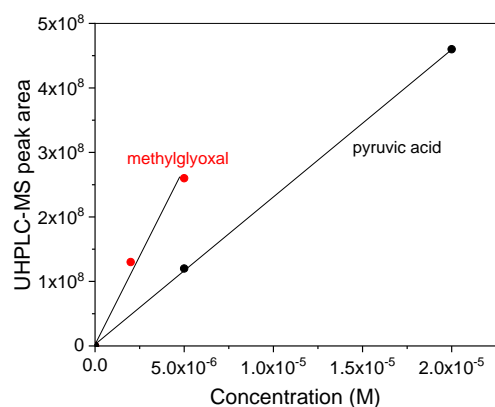
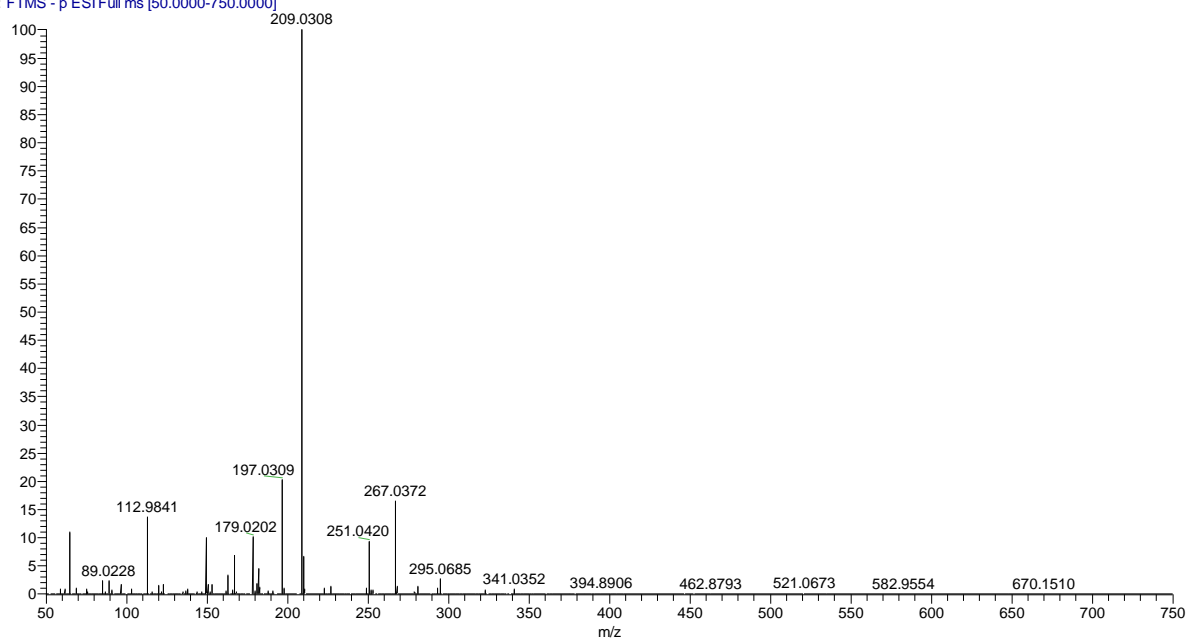


Figure SI-3 : UHPLC-MS of DNPH derivatives

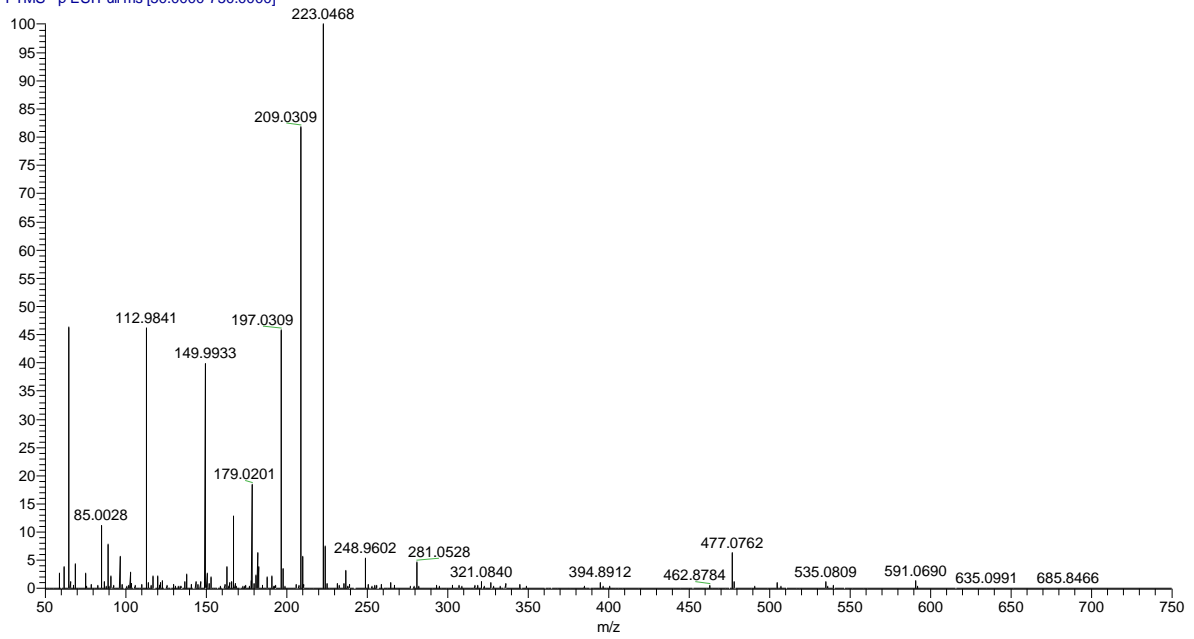
m/z = 209.0309

Daide-DNPH-3 #614 RT: 5.04 AV: 1 NL: 5.76E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



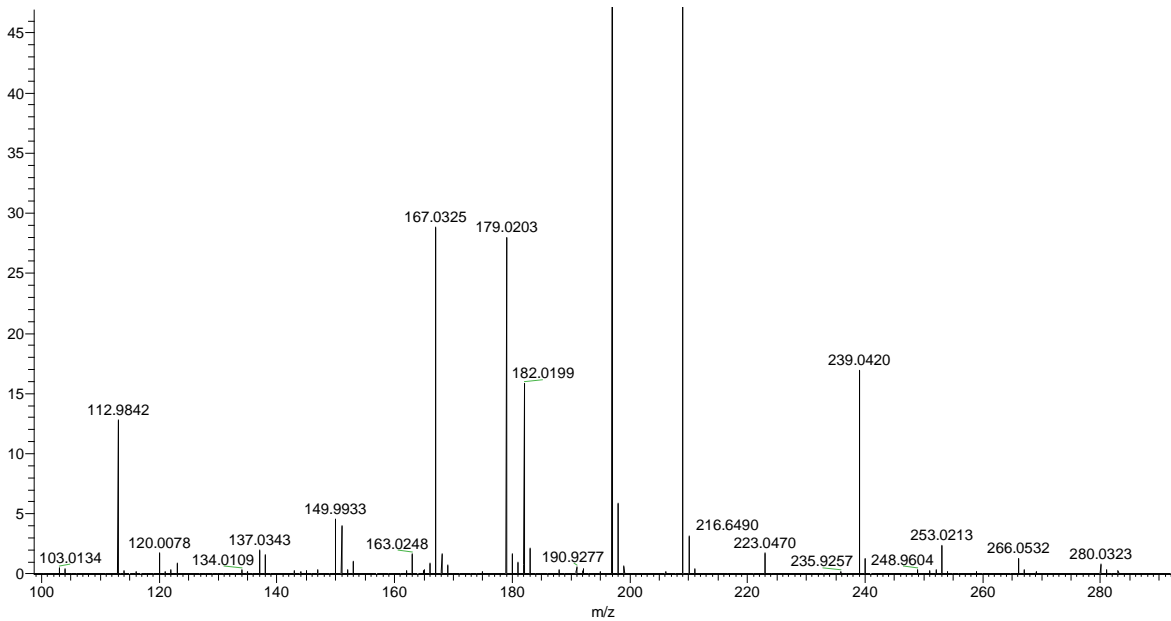
m/z = 223.0468

Daide-DNPH-3 #666 RT: 5.46 AV: 1 NL: 1.82E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



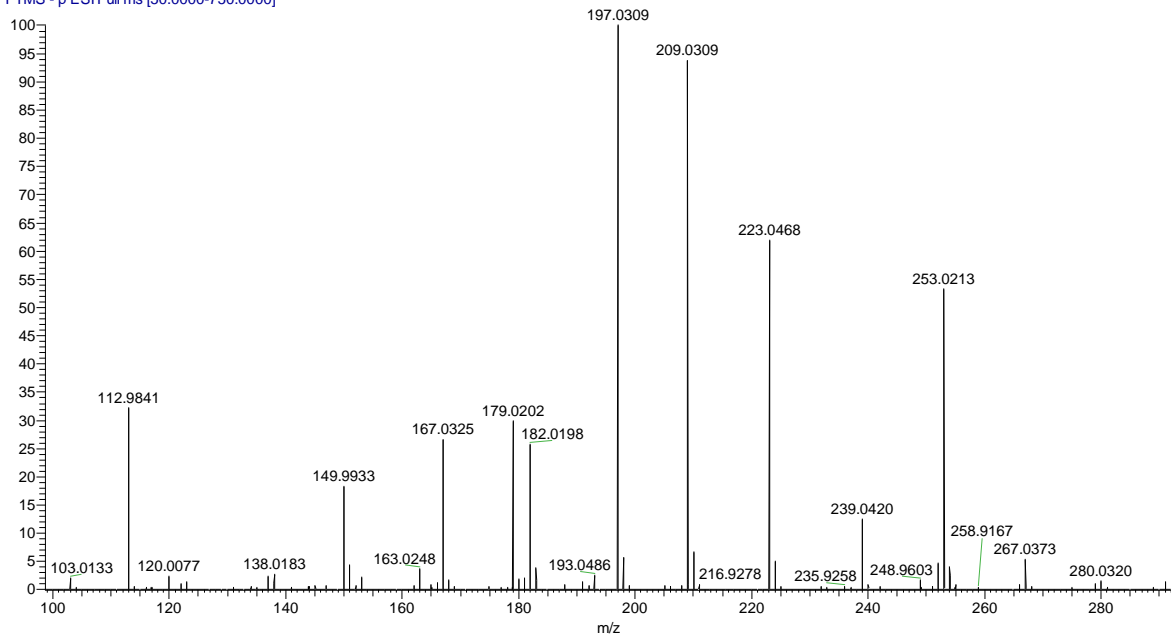
m/z = 239.0422

Daide-DNPH-3 #522 RT: 4.29 AV: 1 NL: 8.56E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



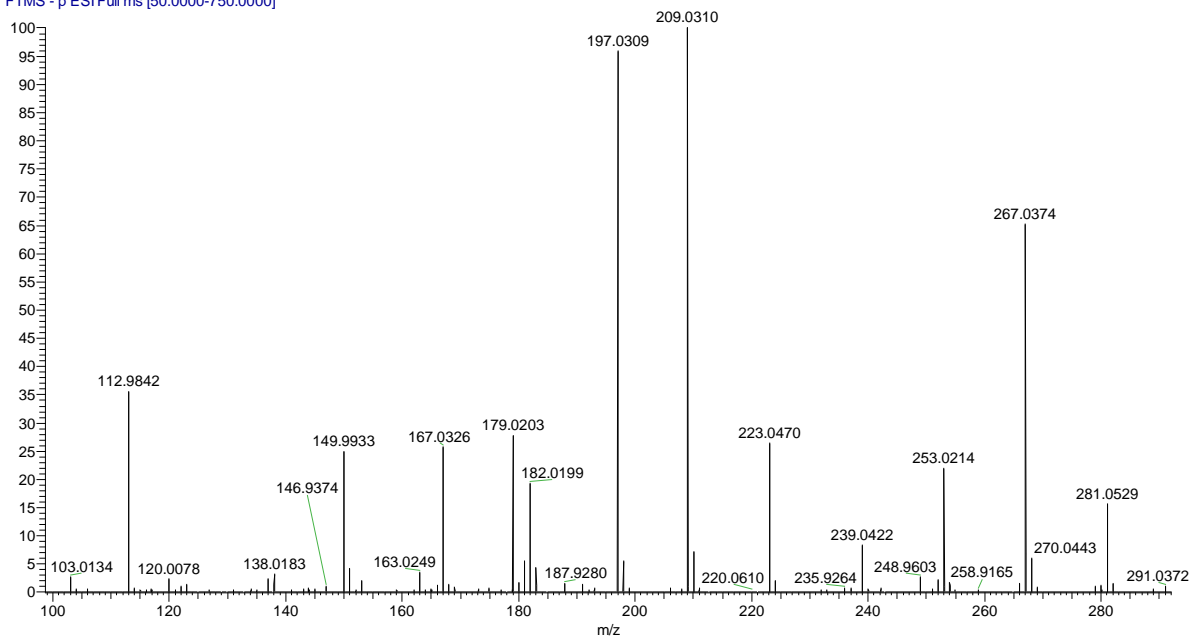
m/z = 253.0213

Davide-DNPH-3 #560 RT: 4.60 AV: 1 NL: 2.22E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



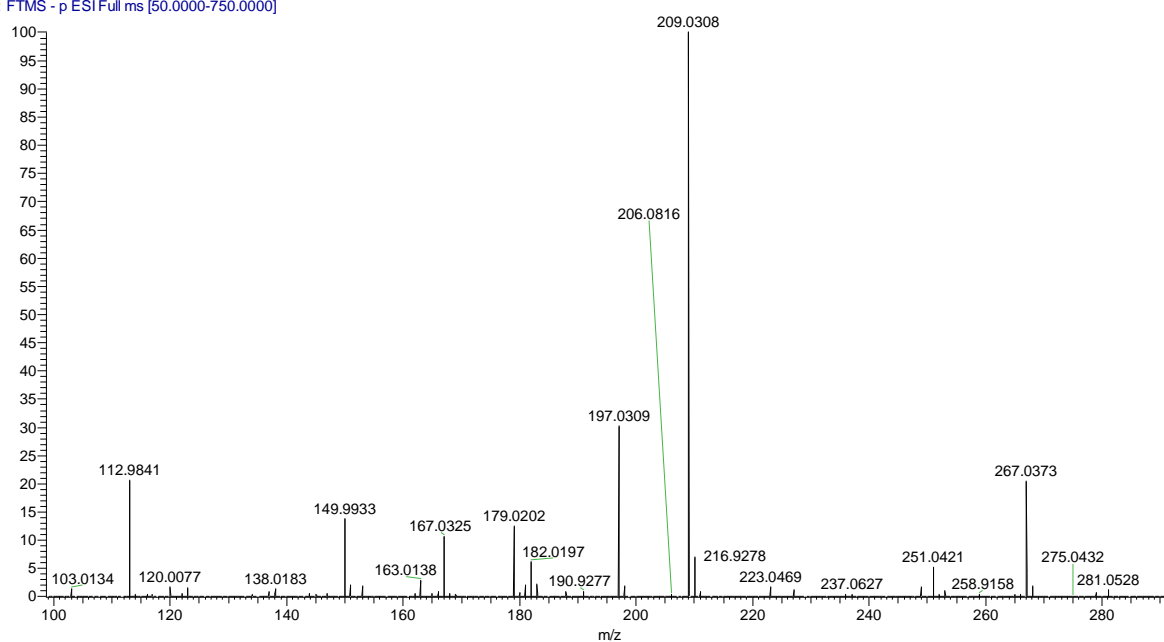
m/z = 267.0374

Davide-DNPH-3 #570 RT: 4.68 AV: 1 NL: 1.97E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



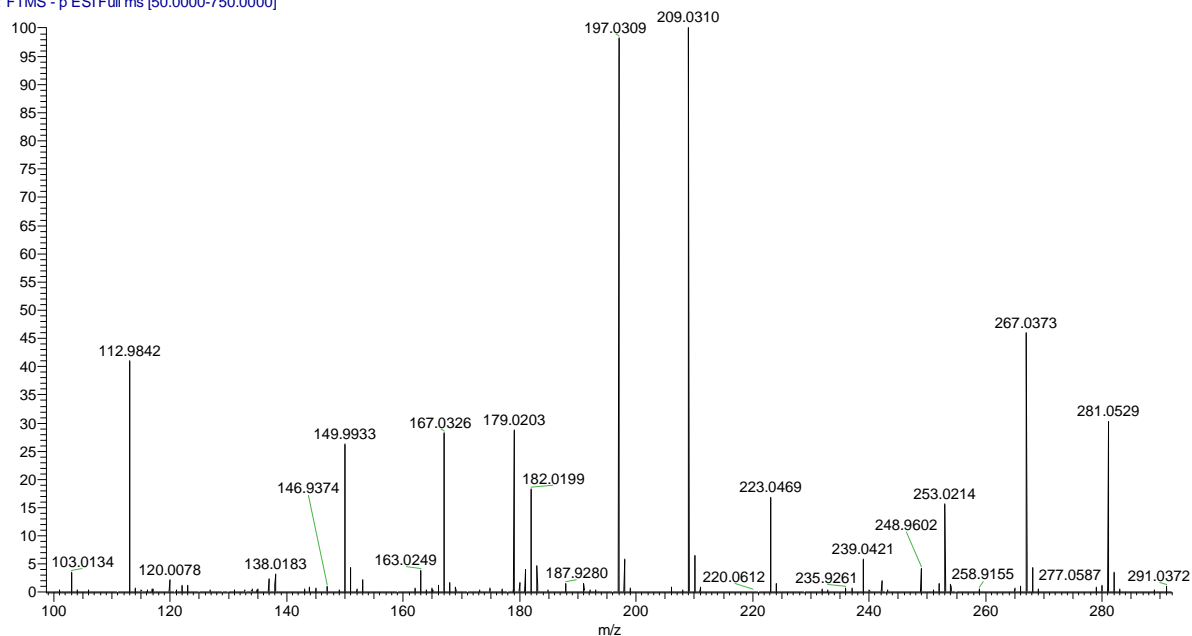
m/z = 265.0581

Davide-DNPH-3 #594-627 RT: 4.87-5.13 AV: 17 NL: 3.86E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



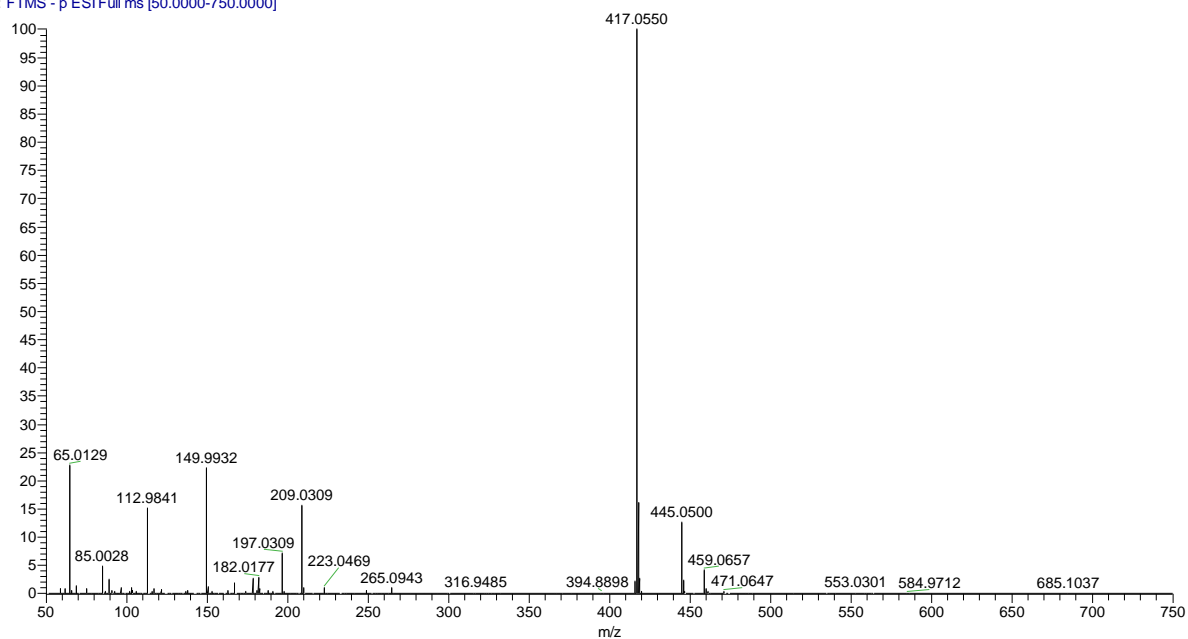
m/z = 281.0529

Davide-DNPH-3 #574 RT: 4.71 AV: 1 NL: 1.90E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



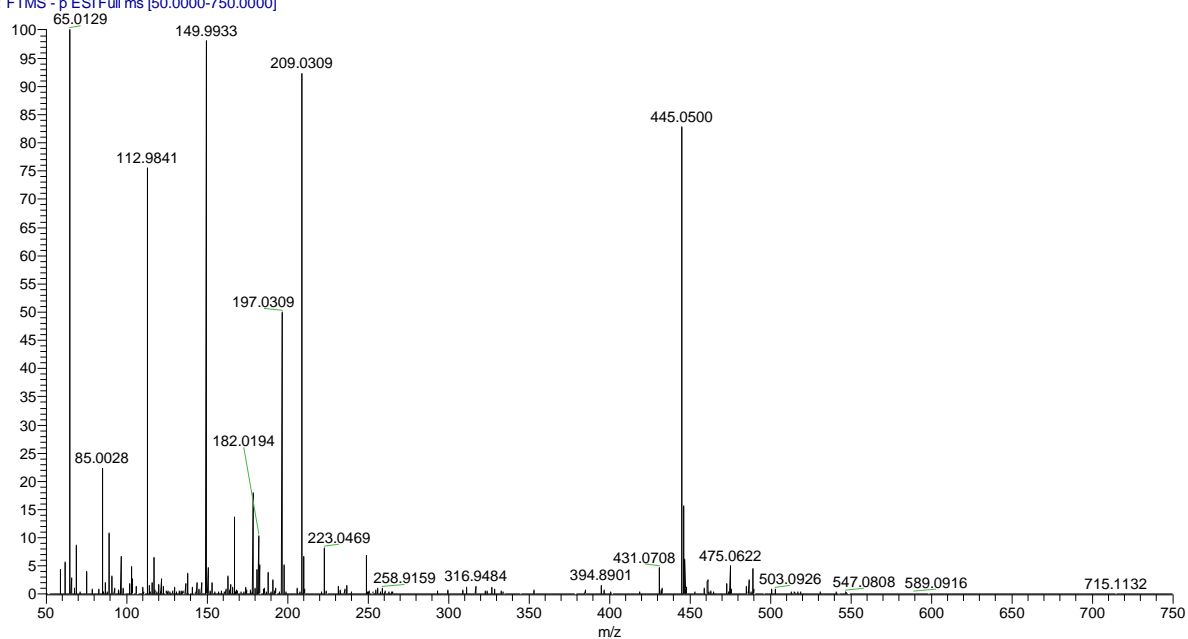
m/z = 417.0551

Davide-DNPH-3 #802 RT: 6.57 AV: 1 NL: 5.78E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



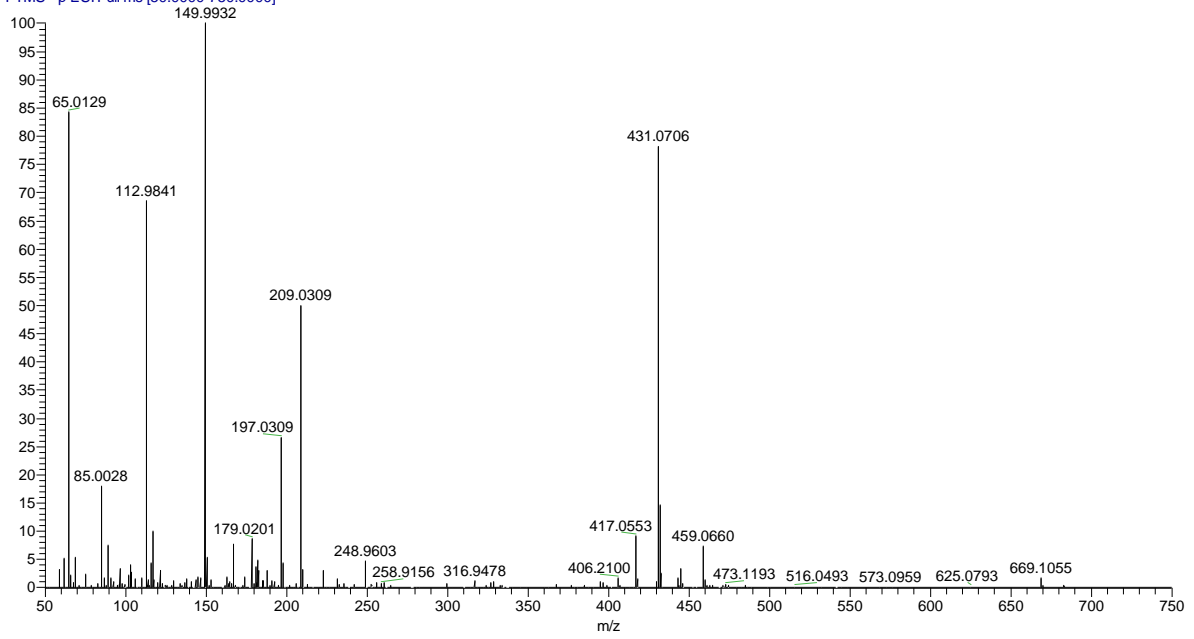
m/z = 445.0499

Davide-DNPH-3 #754 RT: 6.18 AV: 1 NL: 1.11E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



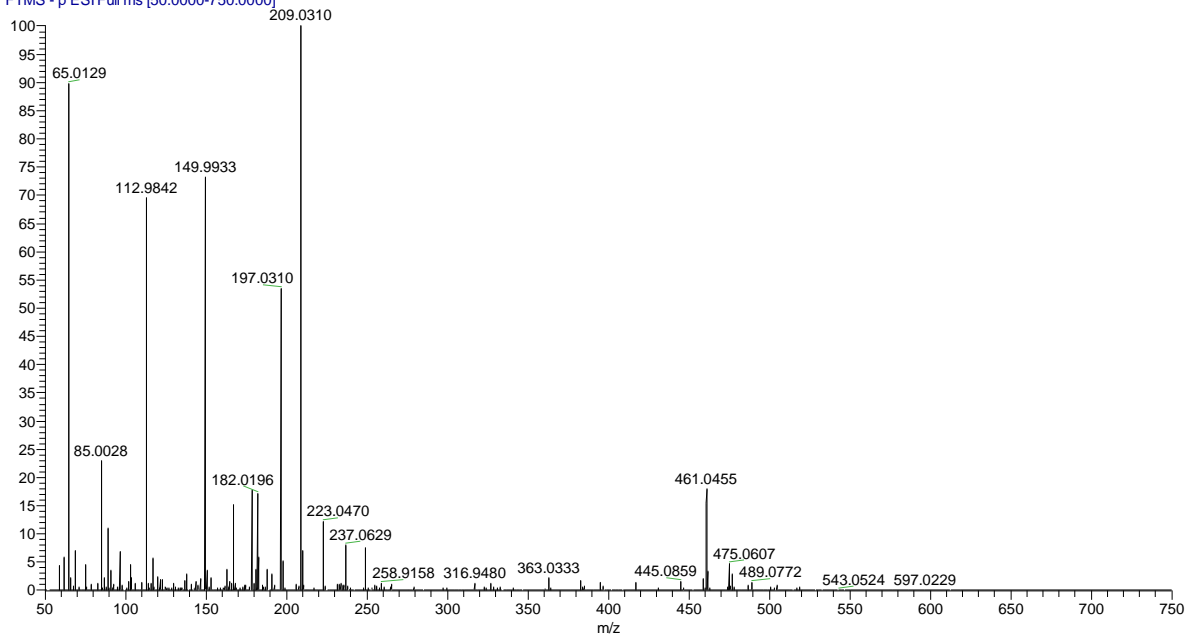
m/z = 431.0709

Davide-DNPH-3 #846 RT: 6.92 AV: 1 NL: 1.74E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



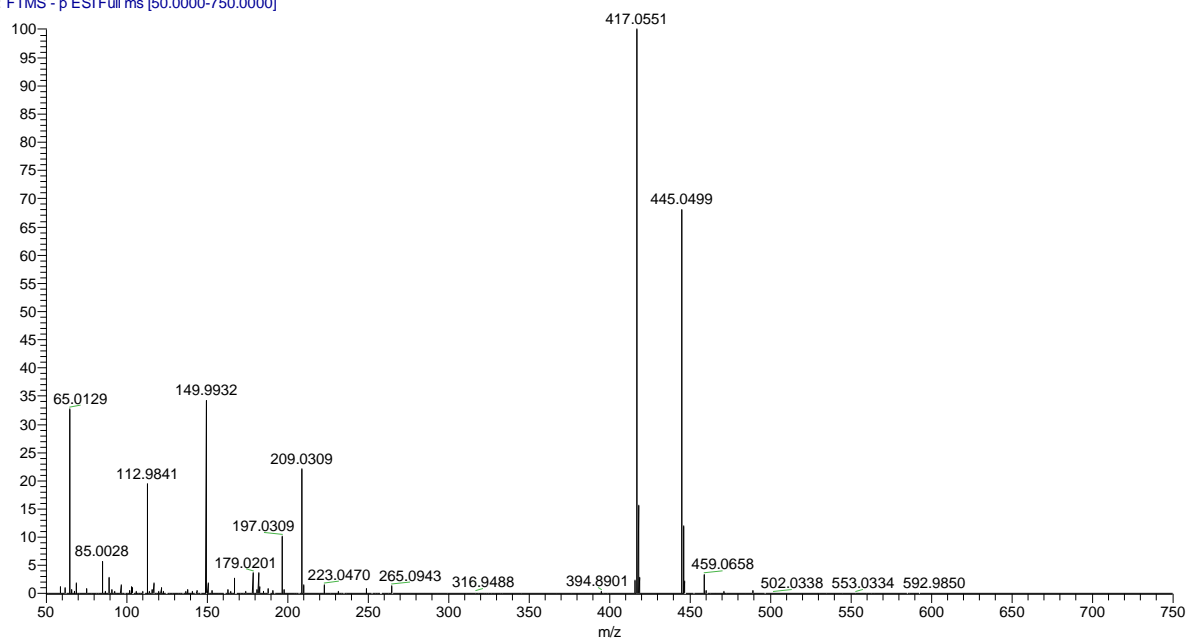
m/z = 461.0455

Davide-DNPH-3 #720 RT: 5.90 AV: 1 NL: 1.17E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



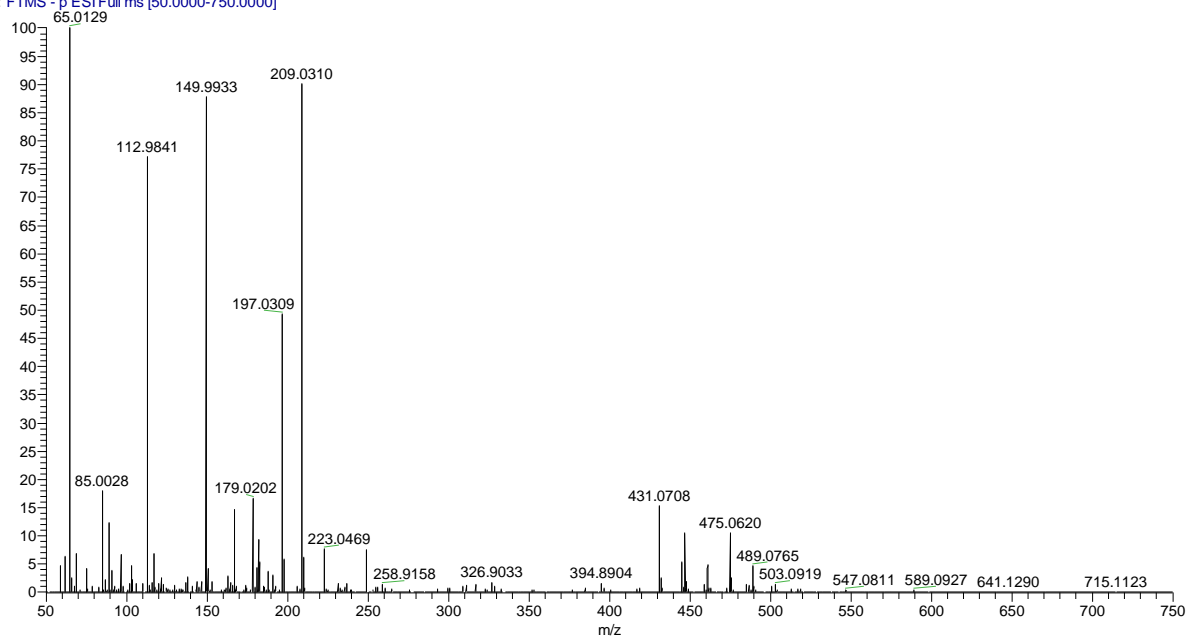
$m/z = 459.0662$

Daide-DNPH-3 #806 RT: 6.60 AV: 1 NL: 4.13E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



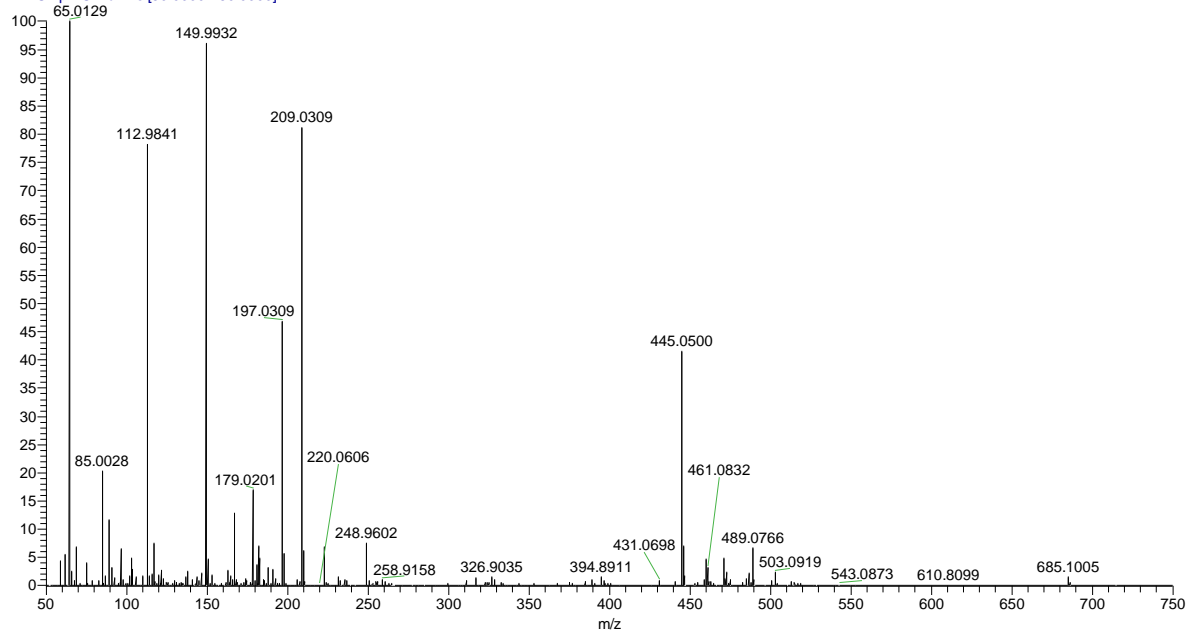
$m/z = 475.0615$

Daide-DNPH-3 #748 RT: 6.13 AV: 1 NL: 1.15E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



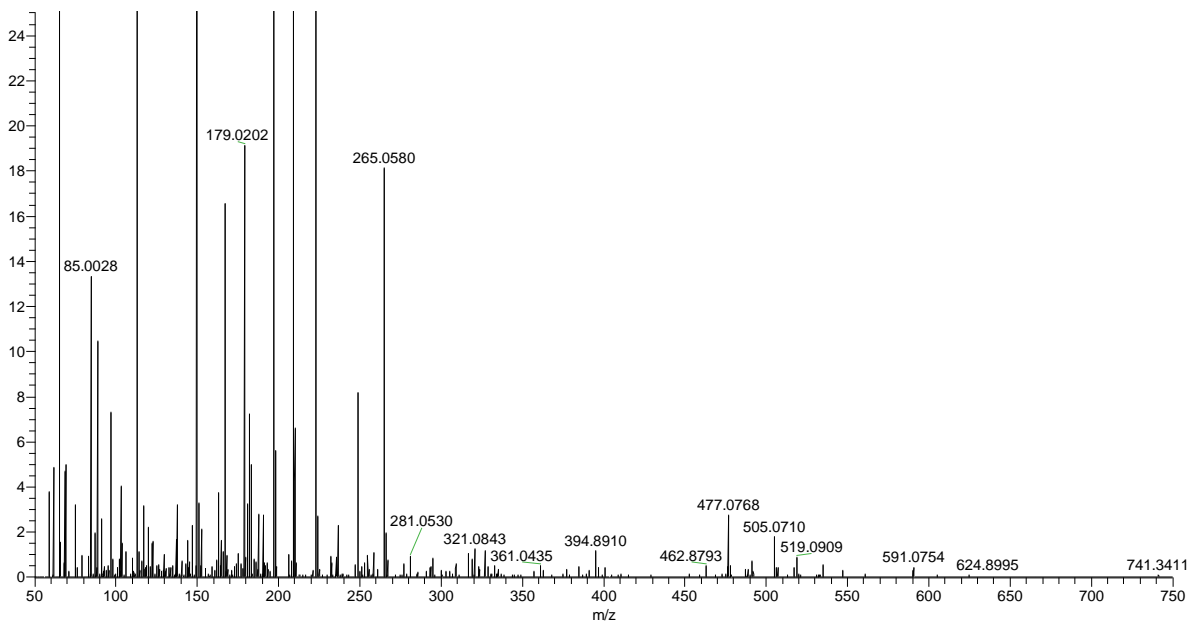
$m/z = 489.0767$

Davide-DNPH-3 #768 RT: 6.29 AV: 1 NL: 1.12E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



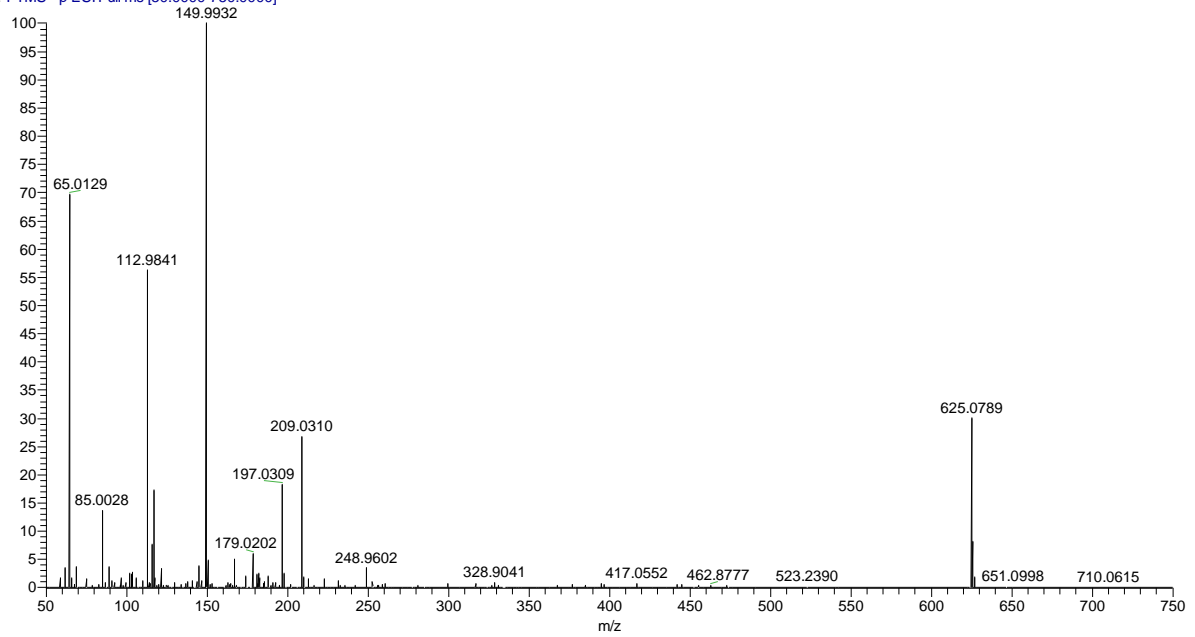
$m/z = 505.0716$

Davide-DNPH-3 #682 RT: 5.59 AV: 1 NL: 1.33E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



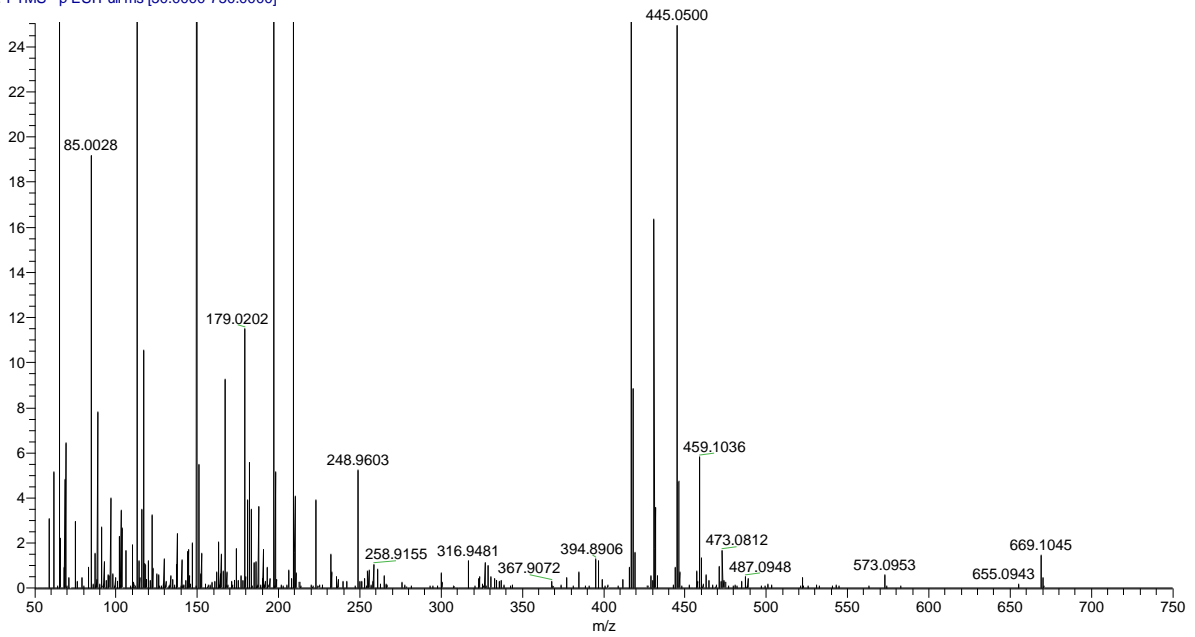
$m/z = 625.0793$

Davide-DNPH-3 #910 RT: 7.44 AV: 1 NL: 2.29E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



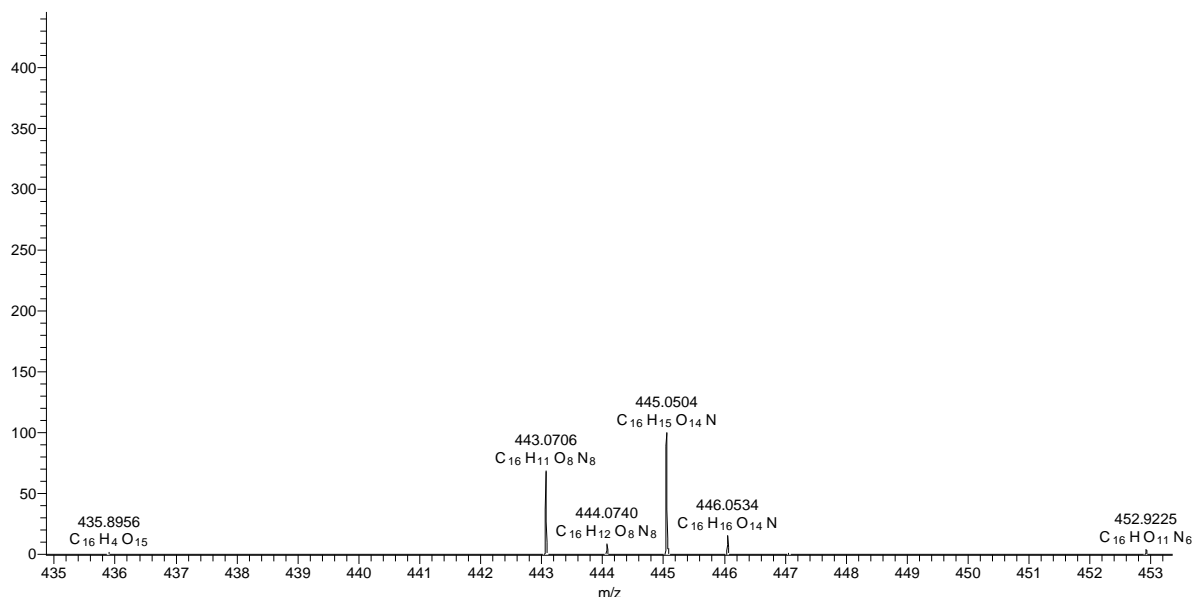
$m/z = 669.1066$

Davide-DNPH-3 #826 RT: 6.76 AV: 1 NL: 1.44E7
T: FTMS - p ESI Full ms [50.0000-750.0000]



m/z = 443.0706

Daide-DNPH-3 #854 RT: 6.99 AV: 1 NL: 6.04E5
T: FTMS - p ESI Full ms [50.0000-750.0000]



Text 3: UHPLC conditions in UHPLC-MS analyses

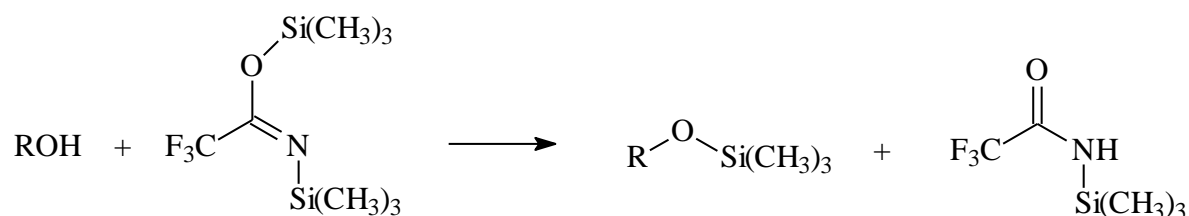
UHPLC separation conditions were the following: The aqueous solvent (A) consisted of a mixture of 0.1% formic acid, and the organic phase (B) was acetonitrile. Separation was achieved with a gradient program consisting of 0–7.5 min 5% and 7.5–8.5 min 99% of mobile phase B. After 8.5 min, the gradient was returned to the initial conditions and the analytical column was reconditioned for 3.5 min. The flow rate was set to 0.450 ml.min⁻¹. The spectrometer operated in negative and positive modes. The formulas are proposed based on ppm < 5.

Text 4: Analysis of carboxylic and hydroxylic intermediates by BSTFA derivatization.

BSTFA derivatization was conducted as follows. A stock solution of SRNOM was prepared at 40 mg.L⁻¹ and neutralized to pH 7±0.2 using NaOH (0.1 M). Six portions of 35 mL were irradiated in the quartz reactor until absorbance at 254 nm declined from 0.85 to 0.35; solutions were then pooled, acidified using HCl (0.1 M), and lyophilised until perfect dryness. Then, 1 mL of acetonitrile was added to the dried powder. The acetonitrile solution was withdrawn, transferred to a GC vial, and finally mixed with 0.3 mL of BSTFA + 1% TMCS.

After immediate sealing and mixing for 30 s, a 1 μL portion was injected in the GC-MS. A reference sample containing non irradiated SRNOM (210 ml at 40 $\text{mg}\cdot\text{L}^{-1}$) was prepared in the same conditions.

The reaction between compounds containing OH (alcohols or carboxylic acids) yields the following silylated derivative that is volatile and detectable by GC-MS :



Compound separation was achieved by an HP-5MS (5% phenyl methyl siloxane) capillary column with 30 m length, 0.25 mm internal diameter, and 0.25 mm film thickness. The injector temperature was set at 250 $^{\circ}\text{C}$ and the injection volume was 1.0 μL (split ratio of 20:1). The GC oven temperature program was: 50 $^{\circ}\text{C}$ for 1 min followed by a gradient of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$ to 250 $^{\circ}\text{C}$ and held for 5 min. Mass spectra were scanned between m/z 50 and m/z 500 with the source temperature set at 230 $^{\circ}\text{C}$. Identification was based on matching query spectra to spectra present in the reference library (NIST17). with a minimum spectral similarity measure of 95%.

Glycolic acid was used as a reference compound for the quantification of the other photoproducts.

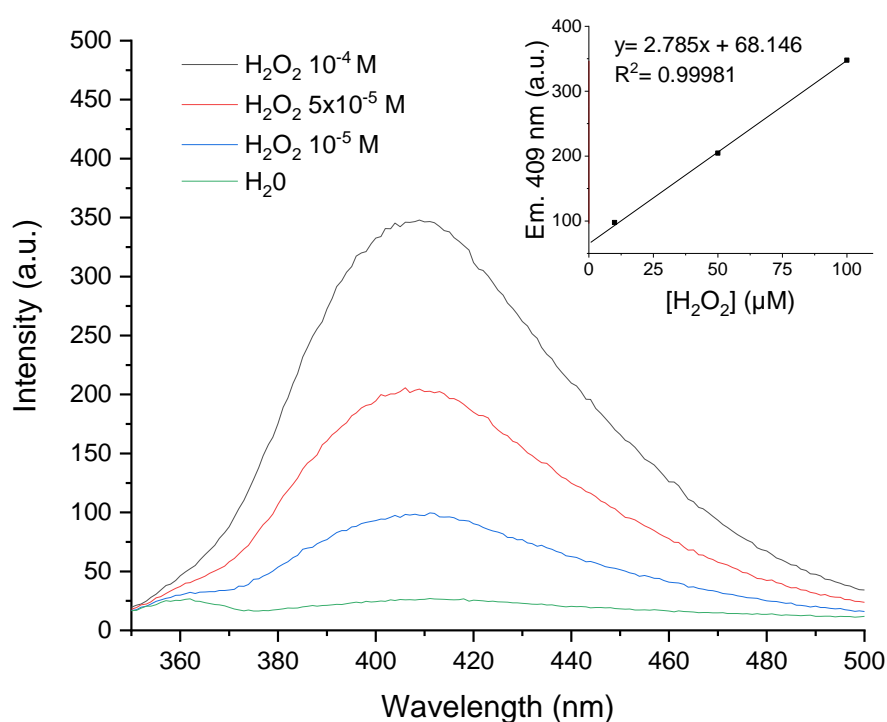
Text 5 : Ionic Chromatography-Mass spectrometry analyses

IC-MS was conducted on a Dionex ICS-6000 interfaced to a Thermo simple quadrupole mass spectrometer from Thermo Scientific. Samples were injected onto a Dionex IonPac AS-11-HC-4 μm 2 \times 250 mm column with a Dionex AG11-HC-4 μm guard column. Elution was done with a KOH step gradient beginning at 1 mM KOH from 0 to 5 min, 30 mM KOH from 5.1 to 25 min, 60 mM KOH from 25.1 to 31 min. 60 mM was held until 35 min, and the column re-equilibrated at 1 mM KOH at 35.1 min at a flow rate of 0.36 $\text{mL}\cdot\text{min}^{-1}$ and 40 $^{\circ}\text{C}$. An electrochemical suppressor was used to neutralize the KOH eluent before reaching the mass spectrometer. The simple quadrupole mass spectrometer was operated in negative ion mode using electrospray ionization with an ESI capillary voltage of 3000 V. Full scan analysis (10-500 m/z over 45 min) and targeted analysis (± 0.5 amu) were done.

Text 6 : Peroxide measurements

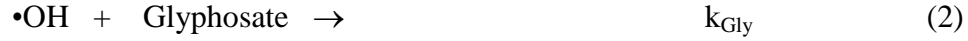
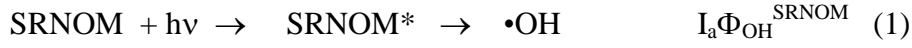
Two mL of a phosphate buffer (pH 7.4) solution of horseradish peroxidase was mixed with 4 mL of 4-hydroxyphenylacetic acid (10^{-3} M) and 60 μ L of sample. The formation of the dimer of 4-hydroxyphenylacetic acid was monitored by fluorescence (excitation wavelength at 320 nm) (Fig SI-4). It allowed to estimate the concentration of $RO_2H + RO_2R + H_2O_2$. To estimate the concentrations of peroxides (RO_2H and RO_2R) only, experiments were repeated by adding catalase in the solution containing 4-hydroxyphenylacetic acid and the sample before the mixing with horseradish peroxidase. The concentration of H_2O_2 was obtained by difference. A calibration curve was drawn by titrating H_2O_2 solutions (1-50 μ M) in presence of SRNOM (20 mg L^{-1}).

Figure SI-4 : Spectrofluorimetric quantification of peroxides . The calibration curve measures the concentration of the dimer of 4-hydroxyphenylacetic acid. The excitation wavelength was set at 320 nm.



Text 7 : Determination of the rate of glyphosate consumption in SRNOM solutions

Based on the following processes :



the rate of glyphosate (R_{Gly}) loss is equal to :

$$R_{\text{Gly}} = k_{\text{Gly}}[\bullet\text{OH}][\text{Gly}]$$

Using that the rate of $\bullet\text{OH}$ formation is equal to its rate of loss once the quasi stationary state is reached, one can write that:

$$I_a\Phi_{\text{OH}}^{\text{SRNOM}} = k_{\text{Gly}}[\bullet\text{OH}]_{\text{qss}}[\text{Gly}] + k_{\text{SRNOM}}[\bullet\text{OH}]_{\text{qss}}[\text{SRNOM}]$$

This gives:

$$[\bullet\text{OH}]_{\text{qss}} = I_a\Phi_{\text{OH}}^{\text{SRNOM}} / k_{\text{Gly}}[\text{Gly}] + k_{\text{SRNOM}}[\text{SRNOM}]$$

This finally gives :

$$R_{\text{Gly}} = I_0 (1 - 10^{-A_{\text{SRNOM}}}) \Phi_{\text{OH}}^{\text{SRNOM}} \frac{k_{\text{gly}} [\text{Gly}]}{k_{\text{gly}} [\text{Gly}] + k_{\text{SRNOM}} [\text{SRNOM}]}$$

Text 8 : Rate of light absorption of a compound in a mixture

The rate of light absorption of I alone is equal to :

$$I_{aI} = I_0 (1 - 10^{-(A_I)})$$

while the rate of light absorption of I in mixture with II, $(I_{aI})^{\text{II}}$, is equal to :

$$(I_{aI})^{\text{II}} = I_0 A_I / (A_I + A_{\text{II}}) (1 - 10^{-(A_I + A_{\text{II}})})$$

Where A_I and A_{II} are the absorbance of I and II respectively.

Table SI-1 : Carboxylic acids and carbohydrates detected in non-irradiated SRNOM by BSTFA derivatization coupled to GC-MS. The number of OH functions correspond to the number of TMS linked to the compound. NDB is the number of double bond.

	Compounds	Number of OH functions	NDB	Name	N°	m/z adduct and fragments
Acids	C ₃ H ₆ O ₄	3	1	Glyceric acid	16	322, 307, 292, 189, 147, 103, 73
	C ₆ H ₁₀ O ₄	2	2	Hexanedioic acid	31	290, 275, 172, 147, 111, 73
	C ₉ H ₁₆ O ₄	2	2	Azelaic acid	38	332, 317, 217, 147, 73
	C ₁₂ H ₂₂ O ₄	2	2	Dodecane-dioic acid	39	374, 357, 217, 147, 73
	C ₁₈ H ₃₄ O ₂	1	2	Oleic acid	40	396, 339, 183, 129, 73
Carbohy-drates	C ₅ H ₁₀ O ₅	4	1	Xylose	29	438, 217, 204, 147, 73
	C ₆ H ₁₂ O ₅	4	1	L-Rhamnose	32	452, 204, 147, 73
	C ₆ H ₁₂ O ₅	4	1	Fucose	33	452, 217, 204, 147, 73
	C ₆ H ₁₂ O ₆	5	1	Glucose	34	540, 217, 204, 147, 73
	C ₆ H ₁₂ O ₆	5	1	Galactose	35	540, 217, 204, 147, 73

Table SI-2: Carboxylic compounds detected in SRNOM_{3H} by BSTFA derivatization coupled to GC-MS and/or by CI coupled to MS. The number of OH functions corresponds to the number of TMS linked to the compound.

Compound	Number of OH functions	NDB	Name	N°	m/z adduct and fragments
CH ₂ O ₂	1	1	Formic acid	2	
C ₂ H ₄ O ₂	1	1	Acetic acid	4	
C ₂ H ₂ O ₄	2	2	Oxalic acid	9	
C ₂ H ₄ O ₃	2	1	Glycolic acid	7	220, 205, 177, 147, 73
C ₃ H ₆ O ₃	2	1	Lactic acid	11	234, 219, 191, 147, 117, 73
C ₃ H ₄ O ₄	2	2	malonic acid	15	248, 233, 147, 73
C ₃ H ₄ O ₅	3	2	Tartronic acid	17	336, 321, 292, 221, 147, 102, 73
C ₃ H ₄ O ₆	4	2	Dihydroxy malonic acid	18	424, 409, 381, 307, 221, 147, 73
C ₄ H ₆ O ₄	2	2	Butanedioic acid	23	262, 247, 147, 73
C ₄ H ₆ O ₅	3	2	Malic acid	25	350, 335, 307, 245, 233, 175, 147, 73
	2	1	4-amino butanoic acid	26	274, 260, 184, 147, 73
C ₅ H ₈ O ₄	2	2	glutaric acid	27	276, 261, 204, 147, 129, 73
C ₆ H ₈ O ₆	3	3	Tricarballic acid	37	392, 377, 302, 259, 217, 185, 107, 73
C ₁₈ H ₃₆ O ₂	1	1	Stearic acid	41	356, 341, 145, 117, 73

Table SI-3: Carbonyls compounds detected by DNPH derivatization and UHPLC-HRMS in irradiated in SRNOM solutions. The number of CO functions corresponds to the number of

Compound	Number of CO functions	NDB	Name	N°	Δ ppm	m/z adduct in ES ⁻
CH ₂ O	1	1	formaldehyde	1	1.9	209.0309
C ₂ H ₄ O	1	1	acetaldehyde	3	2.8	223.0469
C ₂ H ₄ O ₂	1	1	glycoaldehyde	5	3.5	239.042
C ₂ H ₂ O ₂	2	2	glyoxal	6	3.1	417.0554
C ₂ H ₂ O ₃	1	2	glyoxylic acid	8	4.5	253.0213
C ₃ H ₄ O ₂	2	2	methylglyoxal	10	2.7	431.0709

DNPH linked to the compound.

$C_3H_4O_3$	1	2	pyruvic acid	12	4.7	267.0374
$C_3H_2O_3$	3	3		13	3.0	625.0793
$C_3H_2O_4$	2	3		14	3.9	461.0454
$C_4H_6O_2$	1	2		19	5.0	265.0581
$C_4H_4O_2$	2	3	butenedial	20	2.1	443.0706
$C_4H_6O_3$	1	2		21	4.6	281.053
$C_4H_4O_3$	2	3		22	2.1	459.0662
$C_4H_4O_4$	2	3		24	3.2	475.0615
$C_5H_6O_4$	3	3		28	4.0	489.0767
$C_5H_6O_6$	2	3		30	3.7	505.0720

Table SI-4 : Concentration of carbonyls (M) in original and irradiated SRNOM

Compound	N°	SRNOM	SRNOM _{1h}	SRNOM _{2h}	SRNOM _{3h}	SRNOM _{4h}
formaldehyde	1	4.6E-06	2.1E-05	1.7E-04	1.2E-04	7.5E-05
glycoaldehyde	5	8.3E-09	4.1E-06	7.8E-06	8.2E-06	8.7E-06
glyoxylic acid	8	5.4E-08	1.4E-05	3.3E-05	2.2E-05	1.3E-05
pyruvic acid	12	5.4E-08	5.3E-06	1.0E-05	1.1E-05	1.2E-05
C ₄ H ₆ O ₂	19	1.2E-08	8.3E-07	1.2E-06	1.0E-06	7.9E-07
glyoxal	6	0.00E+00	5.1E-06	2.0E-05	2.3E-05	2.5E-05
methylglyoxal	10	1.4E-07	2.5E-06	5.1E-06	7.6E-06	8.9E-06
C ₃ H ₂ O ₃	13	1.1E-07	1.7E-06	1.1E-05	1.6E-05	2.0E-05
C ₃ H ₂ O ₄	14	0.00E+00	8.0E-07	2.8E-06	2.5E-06	5.8E-07
butenedial	20	0.00E+00	0.00E+00	8.3E-08	1.8E-07	7.1E-08
C ₄ H ₄ O ₃	22	0.00E+00	7.5E-07	7.1E-07	3.1E-06	1.2E-06
C ₄ H ₄ O ₄	24	0.00E+00	2.9E-07	3.1E-07	9.6E-07	3.9E-07
C ₅ H ₆ O ₄	28	0.00E+00	0.00E+00	4.2E-07	6.2E-07	5.0E-07
C ₅ H ₆ O ₆	30	0.00E+00	3.6E-08	1.1E-07	2.6E-07	1.7E-07
C ₃ H ₂ O ₃	13	0.00E+00	0.00E+00	7.5E-07	3.4E-06	5.0E-06

Table SI-5 : Concentration of carboxylic acids in SRNOM and SRNOM_{3h}

Compound	N°	SRNOM		SRNOM _{3h}	
		CI	BSTFA	CI	BSTFA
Formic acid	2	traces	nd	traces	nd
Acetic acid	4	1.57E-7	nd	1.12E-6	nd
Glycolic acid	7	3.85E-7	nd	1.39E-6	9.11E-7
Oxalic acid	9	3.07E-6	nd	6.42E-6	nd
Lactic acid	11		nd	nd	4.80E-7
Malonic acid	15	1.65E-7	nd	1.66E-6	1.12E-6
Tartronic acid	17	traces	nd	4.49E-7	1.57E-7
Dihydroxymalonic acid	18	6.70E-8	nd	1.05E-6	1.10E-7
Butanedioic acid	23	7.08E-7	nd	1.77E-6	1.32E-6
Malic acid	25	4.07E-7	nd	2.09E-6	2.80E-6
Glutaric acid	27	traces	nd	1.17E-7	5.36E-8
Tricarballic acid	37	traces	nd	1.80E-6	2.23E-7