Supporting Information:
Effects of temperature and relative humidity on photochemistry inside secondary organic aerosol materials

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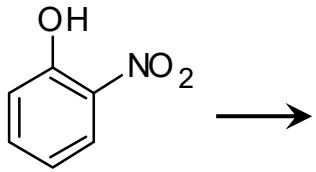
Experimental: LC-PDA-MS

The products of photolysis of 2,4-DNP in isopropanol were analyzed using liquid chromatography (LC) coupled to a photodiode array (PDA) detector and an electrospray ionization (ESI) high-resolution mass spectrometer (MS).[67] Isopropanol was used as the solvent in this analysis because it allowed for a simpler spectrum than SOM would have, as SOM is very complex and is made up of many different molecules that would yield a complicated background spectrum.[29] The LC-PDA-ESIMS instrument consisted of a Surveyor Plus system (including LC pump, autosampler and PDA detector), a standard IonMAX^{TM} ESI source, and a high resolution LTQ-Orbitrap mass spectrometer (all modules are from Thermo Electron, Inc). The separation was performed on a reverse-phase column (Luna C18, 2×150 mm, 100 Å pore size, 5 µm particles, Phenomenex, Inc.). Gradient elution was performed by H_2O/CH_3CN eluent at pH =3 at a flow rate of 200 µL min^{-1}: 0-3 min hold at 10% of CH_3CN, 3-43 min linear gradient to 90% CH_3CN, 43-50 min hold this level, 50-51 min back to 10% CH_3CN, and hold until 70 min. The signals of PDA were acquired over the range of 200 to 700 nm. The ESI setting were: -3.5 kV spray potential, 35 units of sheath gas flow, 10 units of auxiliary gas flow, and 8 units of sweep gas flow.

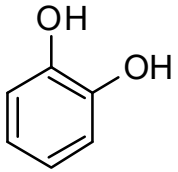
Figure S1

Known Photolysis Products of 2-Nitrophenol (2-NP)

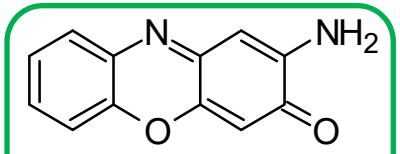
To predict what products could be expected during photolysis of 2,4-DNP it is instructive to examine products from photolysis of related species such as 2-nitrophenol (2-NP) and nitrobenzene (NB). The following products were reported by **Alif et al. (1991)** during aqueous photolysis of 2-NP:



2-nitrophenol

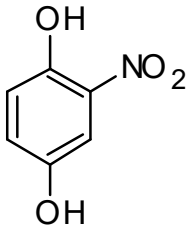


catechol

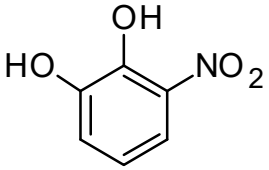


2-aminophenoxazone

Alif et al. were surprised to see 2-aminophenoxazone (because they failed to observe the required amine intermediate) but it was definitively there, confirmed by NMR.

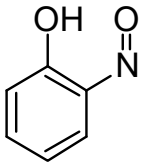


2-nitrohydroquinone

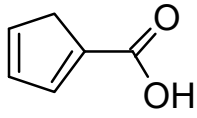


3-nitrocatechol

Dihydroxynitrobenzene products were a result of OH + 2-NP chemistry; they were not formed in the presence of ethanol. Since our experiments were carried out in isopropanol, we did not initially expect to see OH chemistry products in our experiments.



2-nitrosophenol



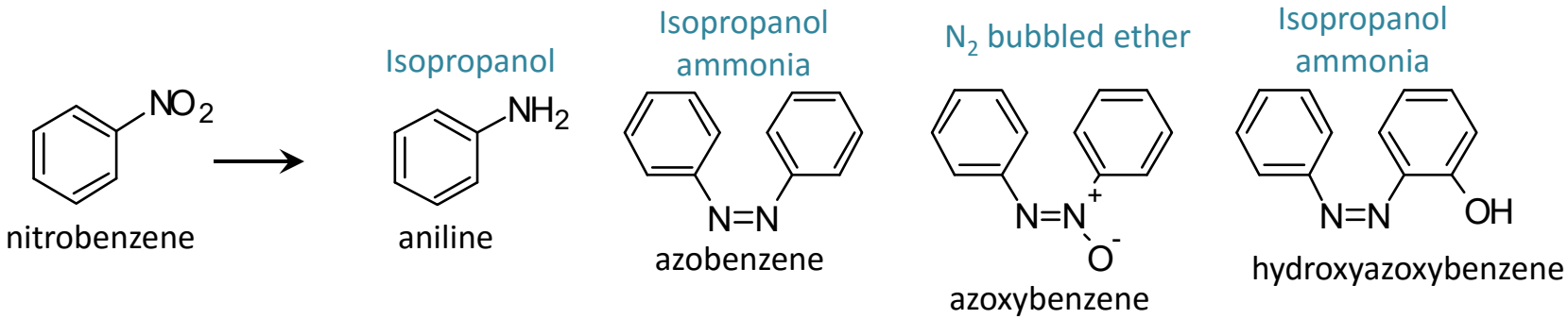
cyclopentadiene carboxylic acids

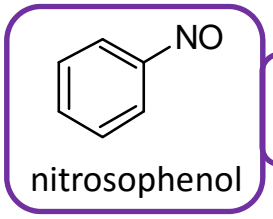
The isomerization product resulting in a C5 ring was suppressed in the presence of alcohols but was important in pure water. We do not expect to see these types of products in our experiments.

Figure S2

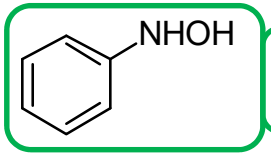
Known Photolysis Products of Nitrobenzene (NB)

To predict what products could be expected during photolysis of 2,4-DNP it is instructive to examine products from photolysis of related species such as 2-nitrophenol (2-NP) and nitrobenzene (NB). The following products were reported by **Barltrop et al. (1967, 1968)** in photolysis of substituted nitrobenzenes in various organic solvents. Solvents serving as good H-atom donors (isopropanol) promoted reduction of $-NO_2$ all the way to $-NH_2$.





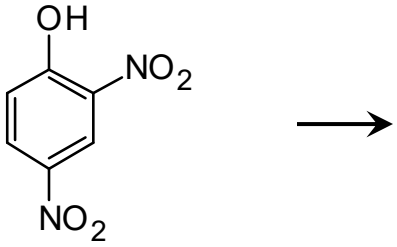
This nitroso compound was not directly observed but suspected as an important intermediate



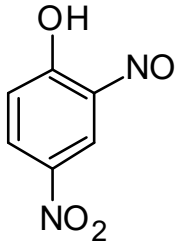
This was also a suspected intermediate, which is supposed to be even less stable than the nitroso compound

Figure S3 Expected and Possibly Observed Monomeric Products of Photolysis of 2,4-DNP

By analogy, the following products could be expected in the photolysis of 2,4-DNP. Species with the expected m/z values appeared in the LC-MS spectra, which suggest (but does not prove) that they were present.

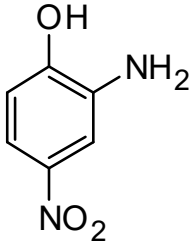


Molecular Formula = $C_6H_4N_2O_5$
[M-H]- = 183.004745 m/z



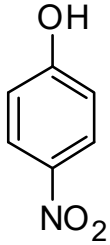
We expected and observed the mass corresponding to this nitroso compound. There should be two structural isomers; indeed two major peaks showed up in the SIM chromatogram. Barltrop et al. did not observe the nitroso compound in their studies, but suspected it as an intermediate.

Molecular Formula = $C_6H_4N_2O_4$
[M-H]- = 167.00983 m/z



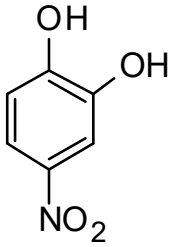
One peak corresponding to this compound was detected. Perhaps only one of the two -NO_2 groups could be fully reduced.

Molecular Formula = $C_6H_6N_2O_3$
[M-H]- = 153.030566 m/z



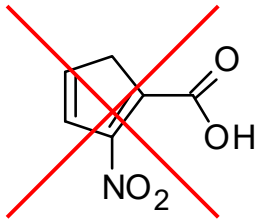
A tiny peak corresponding to this product showed up in the mass spectrum. There appeared to be two peaks in the chromatogram corresponding to the two possible lost -NO_2 groups

Molecular Formula = $C_6H_5NO_3$
[M-H]- = 138.019667 m/z



SIM chromatograms provided evidence for the formation of two isomers of this product. It is not as absorbing as the amine and nitroso products. We did not expect these products based on the studies by Barltrop et al.; indeed the peaks are quite small. See pages 9 & 10.

Molecular Formula = $C_6H_5NO_4$
[M-H]- = 154.01458 m/z



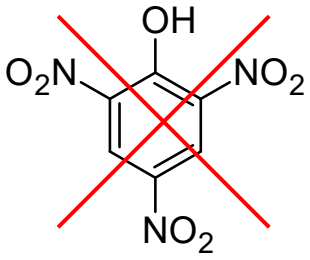
There is a caveat that loss of -NO_2 group followed by isomerization could give a product with the same *m/z* ratio. However, Alif et al. (1991) reported that these products do not form when alcohols are present. We did not observe this product.

Molecular Formula = $C_6H_5NO_4$
[M-H]- = 154.014581 m/z

Figure S4 **Expected and Possibly Observed Monomeric Products of Photolysis of 2,4-DNP**

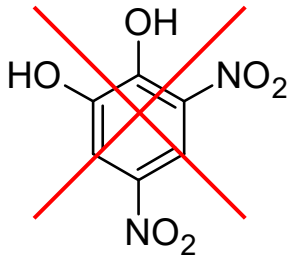
The following products could also be expected in photolysis of 2,4-DNP but we see no evidence of these products in the mass spectrum.

This would have resulted from nitration of 2,4-DNP



Molecular Formula = $C_6H_3N_3O_7$
[M-H]- = 227.989823 Da

This would have resulted from OH addition to 2,4-DNP

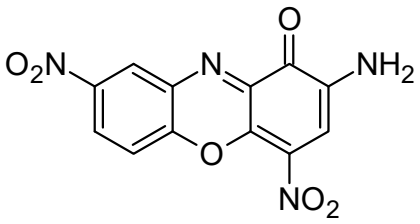


Molecular Formula = $C_6H_4N_2O_6$
[M-H]- = 198.999659 Da

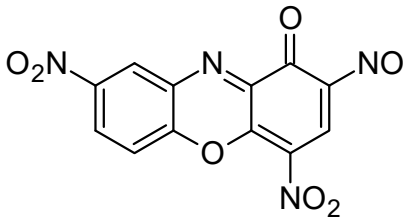
Figure S5

Expected and Possibly Observed Dimeric Products of Photolysis of 2,4-DNP

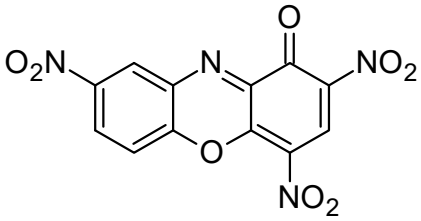
The following dimeric products could also be expected in photolysis of 2,4-DNP. However, only structure boxed in red is a possible match to the observed *m/z* of the eluting ions.



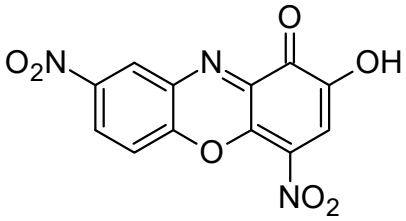
Molecular Formula = $C_{12}H_6N_4O_6$
[M-H]- = 301.021457 Da



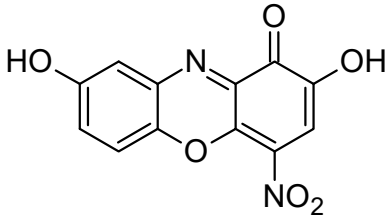
Molecular Formula = $C_{12}H_4N_4O_7$
[M-H]- = 315.000722 Da



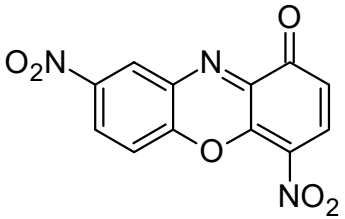
Molecular Formula = $C_{12}H_4N_4O_8$
[M-H]- = 330.995637 Da



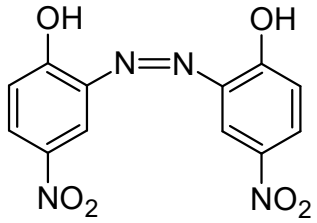
Molecular Formula = $C_{12}H_5N_3O_7$
[M-H]- = 302.005473 Da



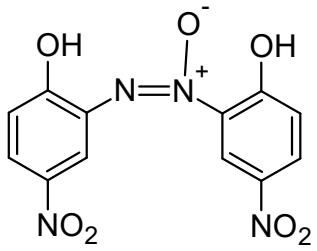
Molecular Formula = $C_{12}H_6N_2O_6$
[M-H]- = 273.015309 Da



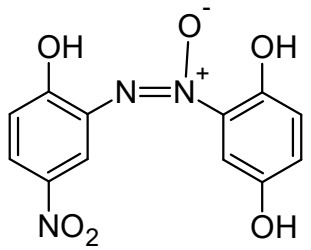
Molecular Formula = $C_{12}H_5N_3O_6$
[M-H]- = 286.010558 Da



Molecular Formula = $C_{12}H_8N_4O_6$
[M-H]- = 303.037108 Da



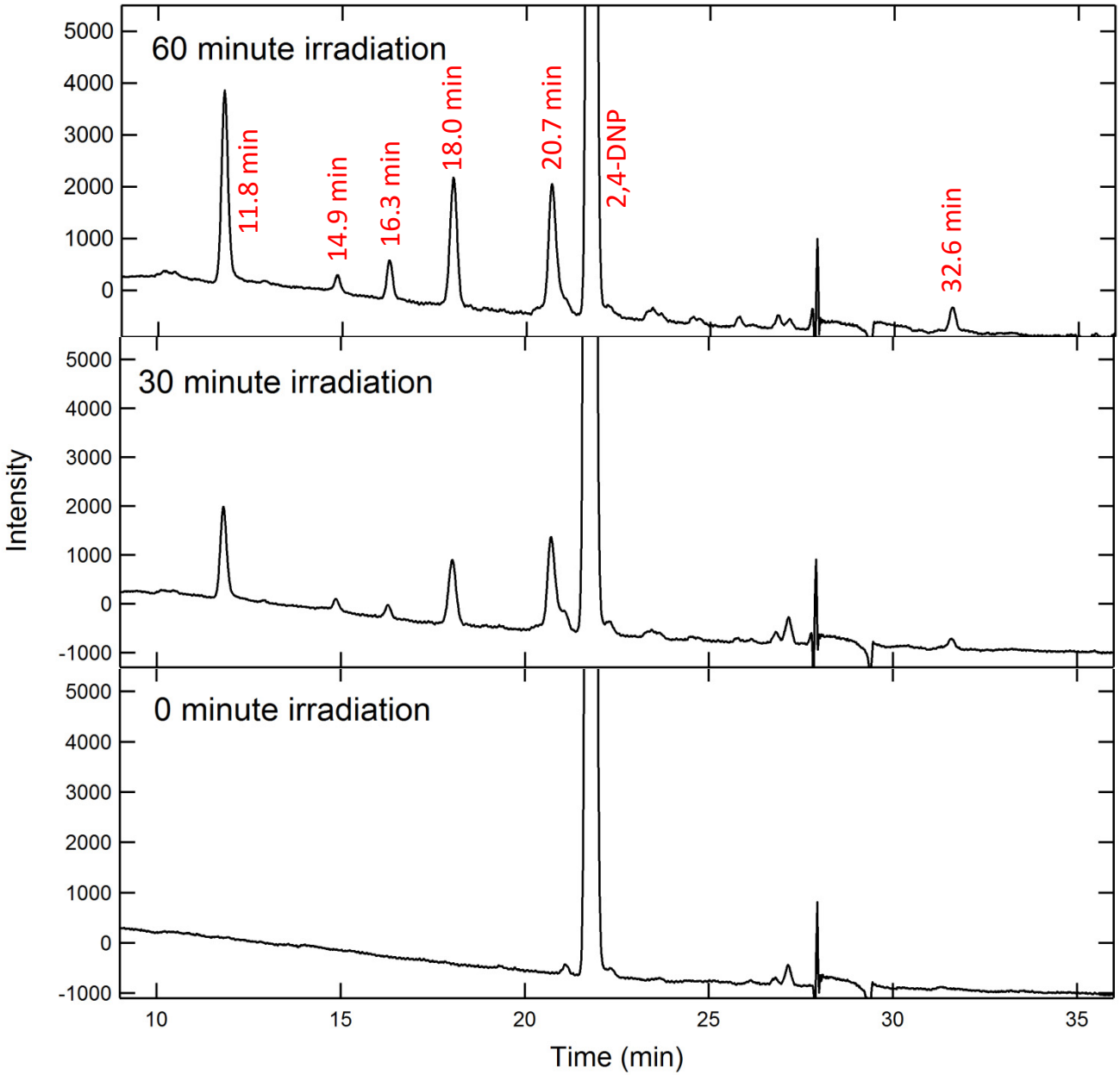
Molecular Formula = $C_{12}H_8N_4O_7$
[M-H]- = 319.032022 Da



Molecular Formula = $C_{12}H_9N_3O_6$
[M-H]- = 290.041859 Da

Figure S6

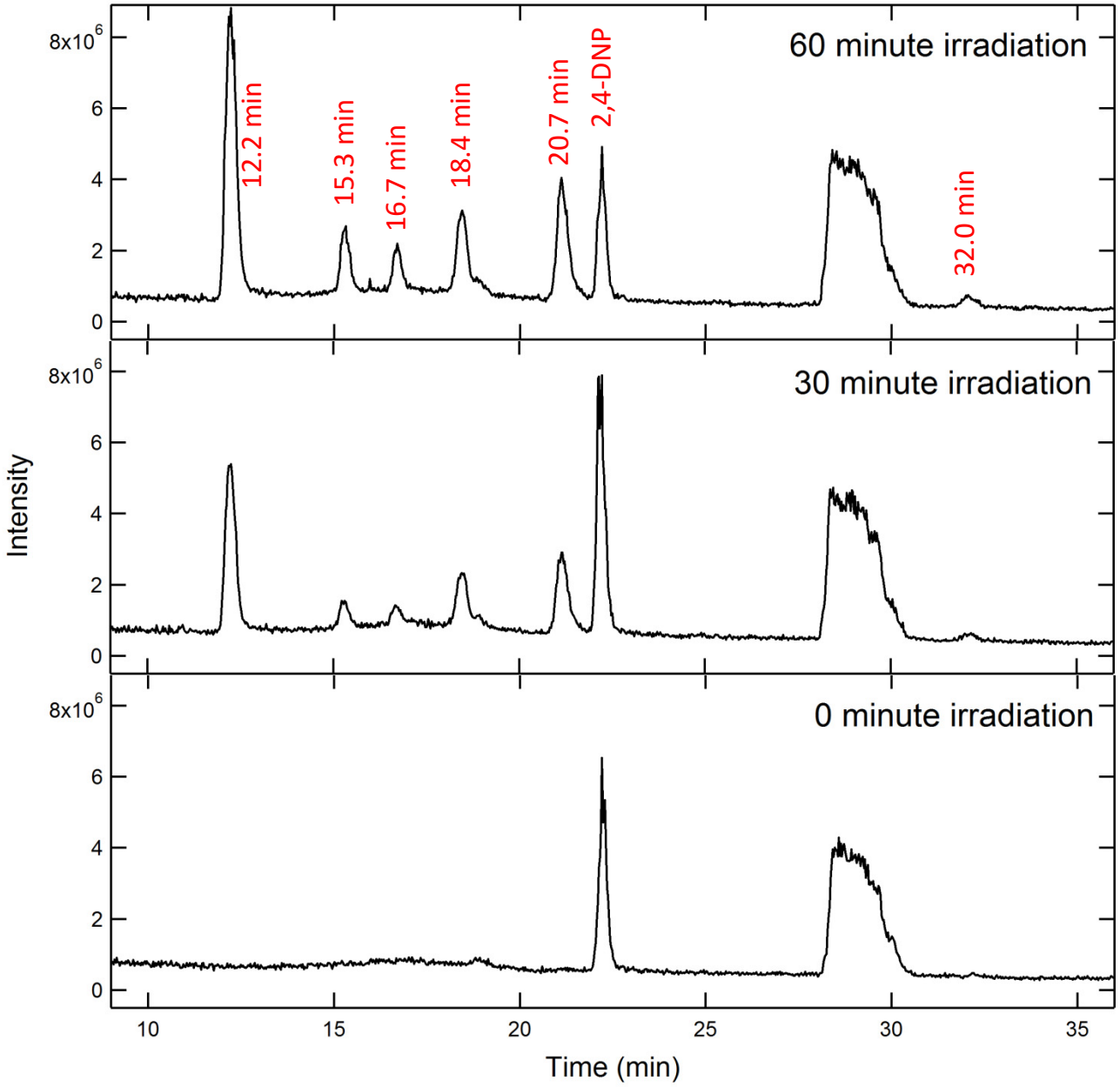
PDA Chromatogram of the Observed Photolysis Products



A sample chromatogram corresponding to 350-500 nm integrated PDA absorbance. There are clear peaks growing at 11.8, 14.9, 16.3, 18.0, 20.7 and 32.6 min in the chromatogram during photolysis. The 11.8, 18.0 and 20.7 min peaks have the correct absorption spectrum characteristics (the corresponding spectra given below) for the expected products, which absorb to the red of 2,4-DNP. The 16.3 min peak is very weak.

Figure S7

MS Chromatograms at Different Photolysis Times



In the MS chromatograms integrated over the 150-170 m/z range, where the majority of products are expected, there is a clear growth of several peaks during photolysis.

Figure S8

PDA vs MS Chromatogram for the 60 min Photolyzed Sample

This is how the MS and PDA chromatograms are correlated with each other. The MS chromatogram corresponds to an integration over the 150-170 *m/z* range. These peaks are also discernible in the TIC spectrum but they are easier to observe in this integration range. The peaks in the MS chromatogram are delayed relative to the corresponding peaks in the PDA chromatogram by about 0.4 min (the time needed for the slow to migrate form the PDA cell into the ESI source).

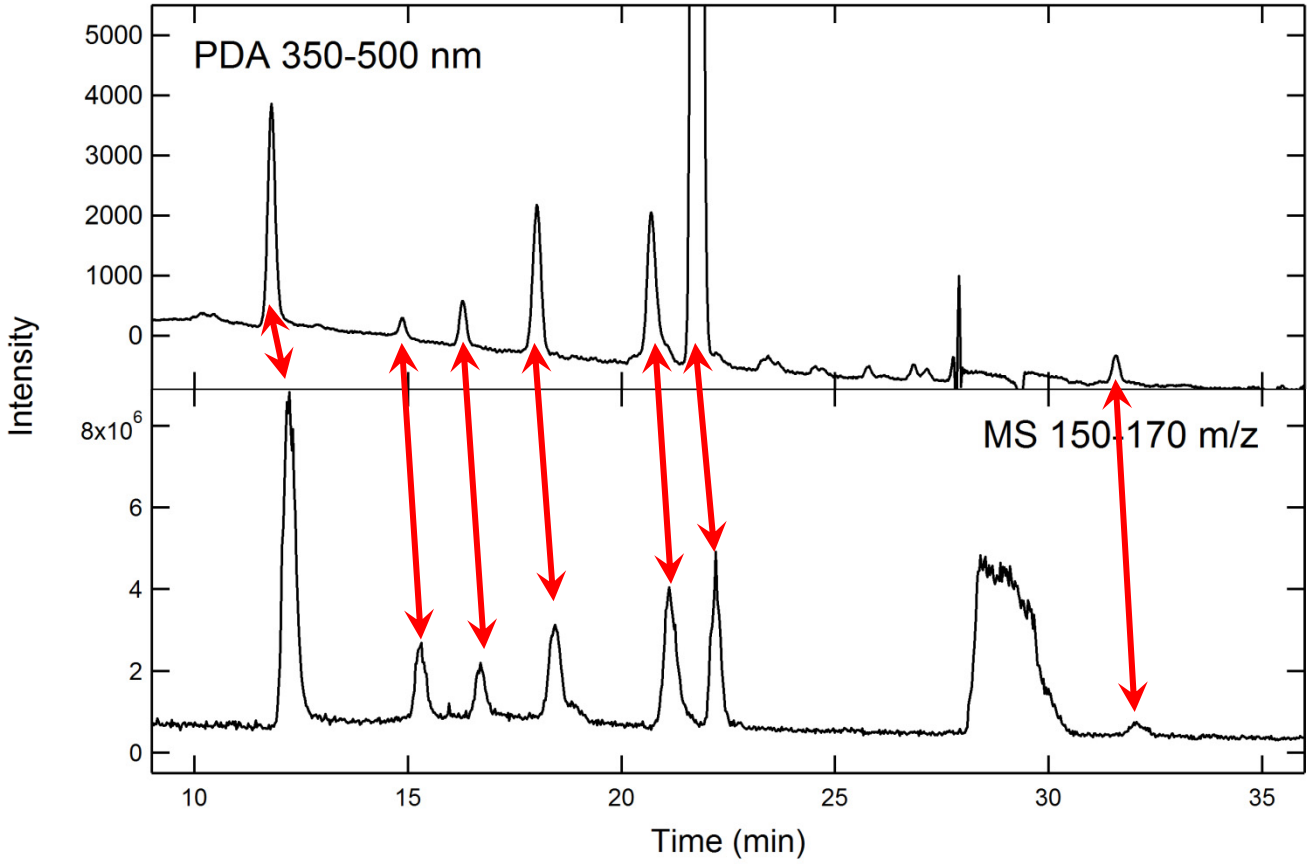
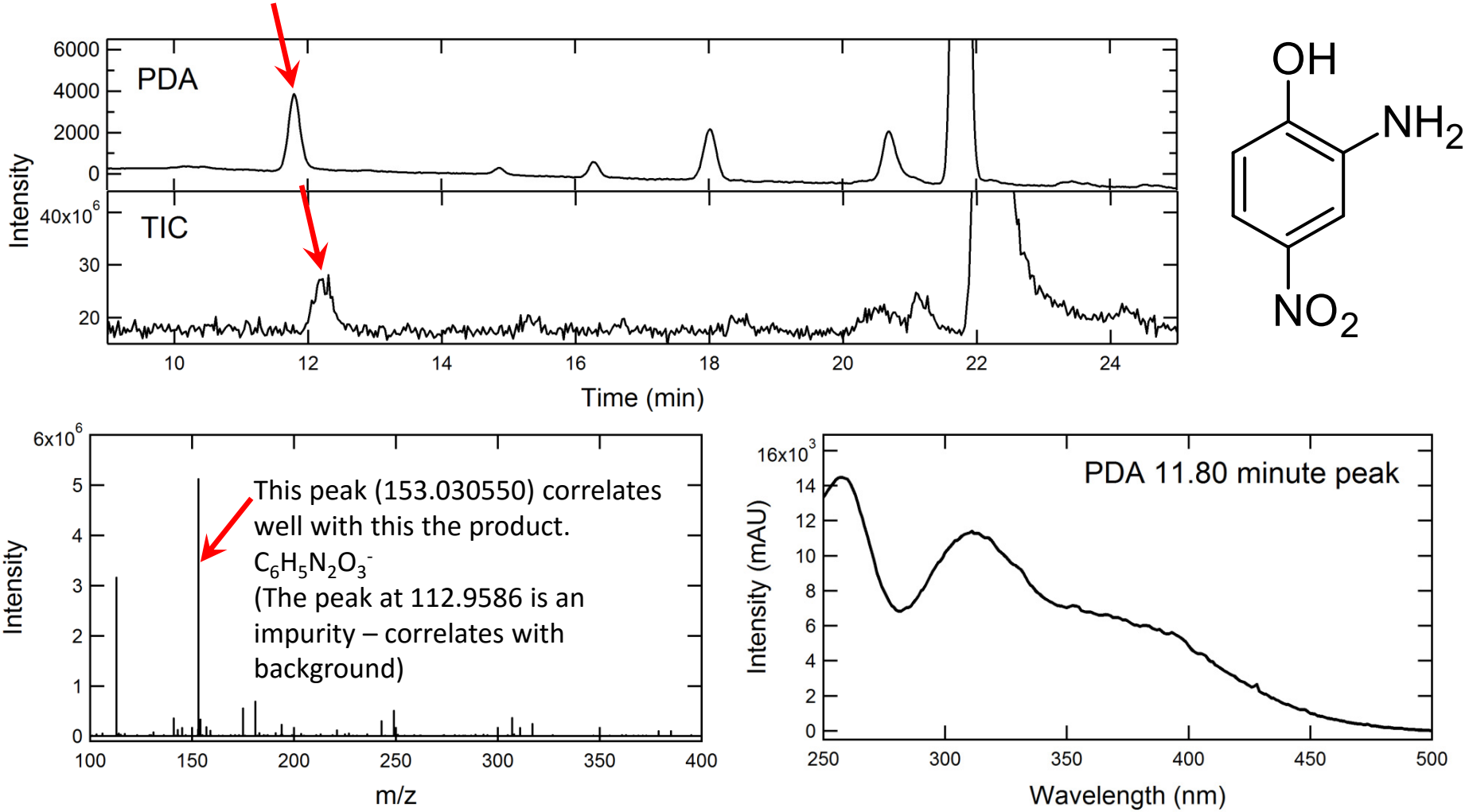


Figure S9

11.8 min peak: chromatagrams, mass spectrum, and absorption spectrum

The 11.8 min peak in the PDA chromatogram correlates to the 12.3 min peak in the MS chromatogram.



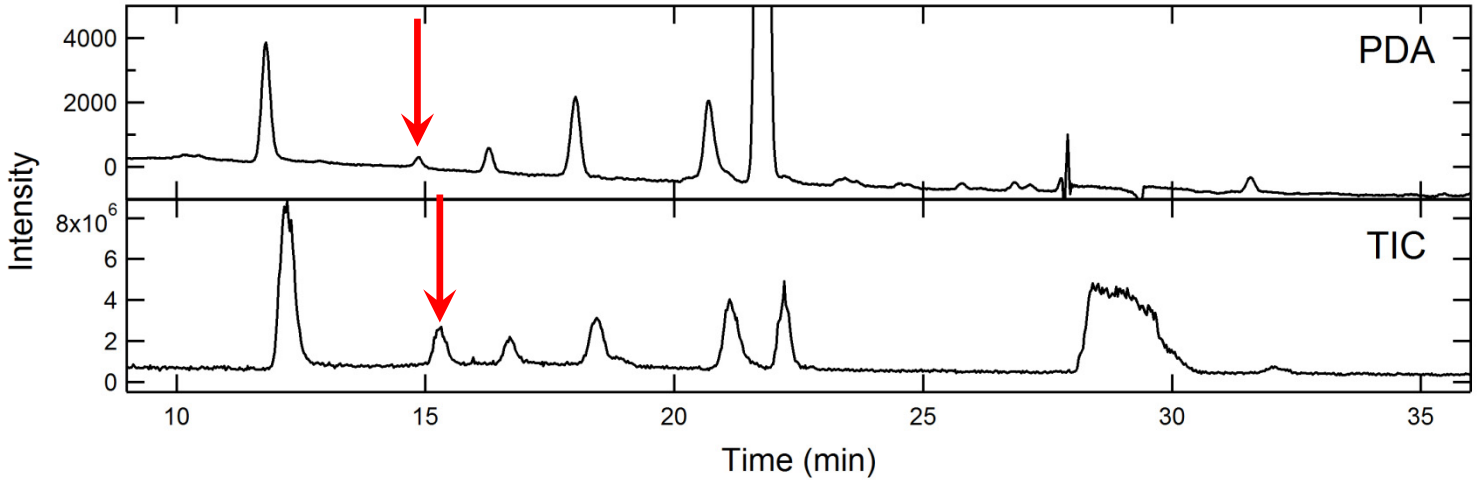
Peak Report for m/z = 153.030550 +/-2.0 ppm

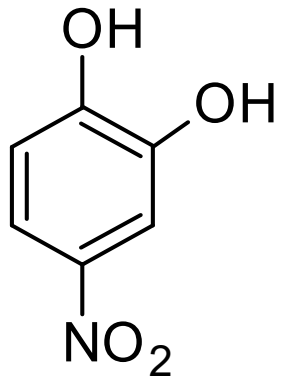
C6 H5 N2 O3 m/z = 153.030566 -0.1 ppm DBE = 6.0

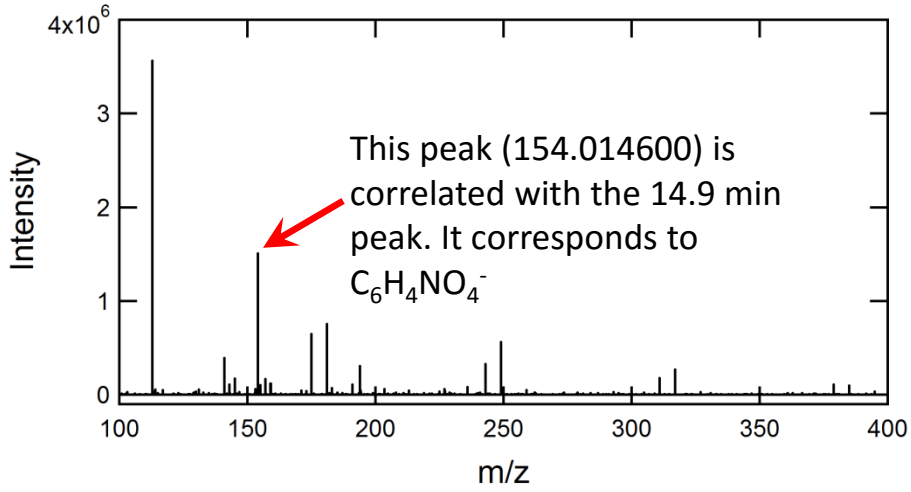
Figure S10

14.9 min peak: chromatagrams, mass spectrum, and absorption spectrum

The 14.9 min peak in the PDA chromatogram correlates to the 15.3 min peak in the MS chromatogram.







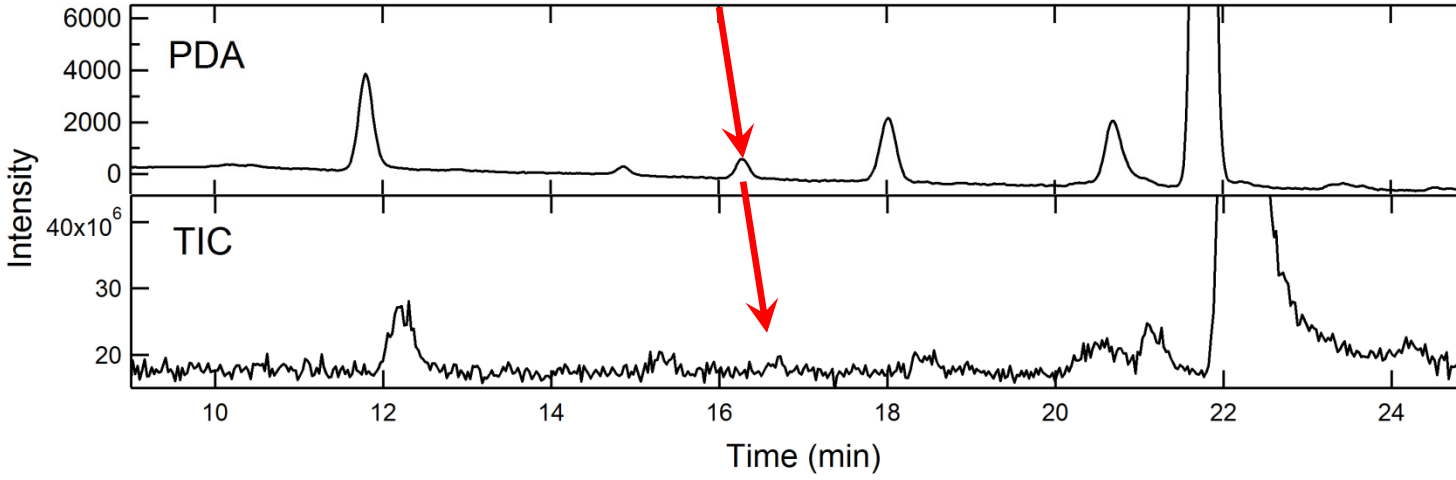
Peak Report for m/z = 154.014600 +/-2.0 ppm

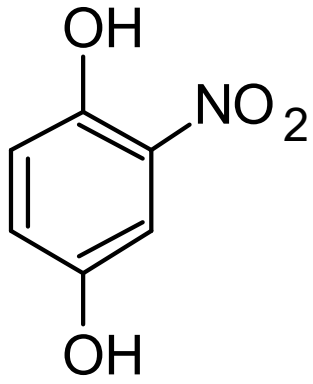
C6 H4 N1 O4 m/z = 154.014581 +0.1 ppm DBE = 6.0

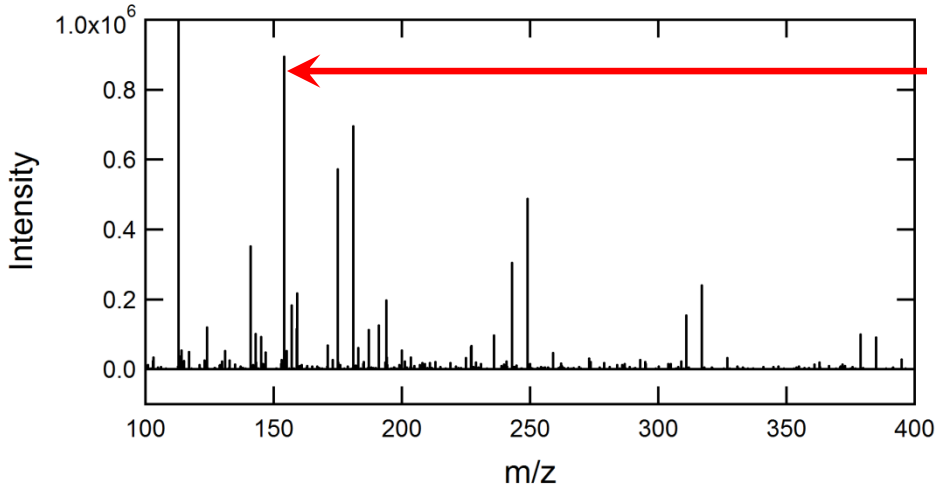
Figure S11

16.3 min peak: chromatagrams, mass spectrum, and absorption spectrum

The 16.3 min peak in the PDA chromatogram correlates to the 16.7 min peak in the MS chromatogram.







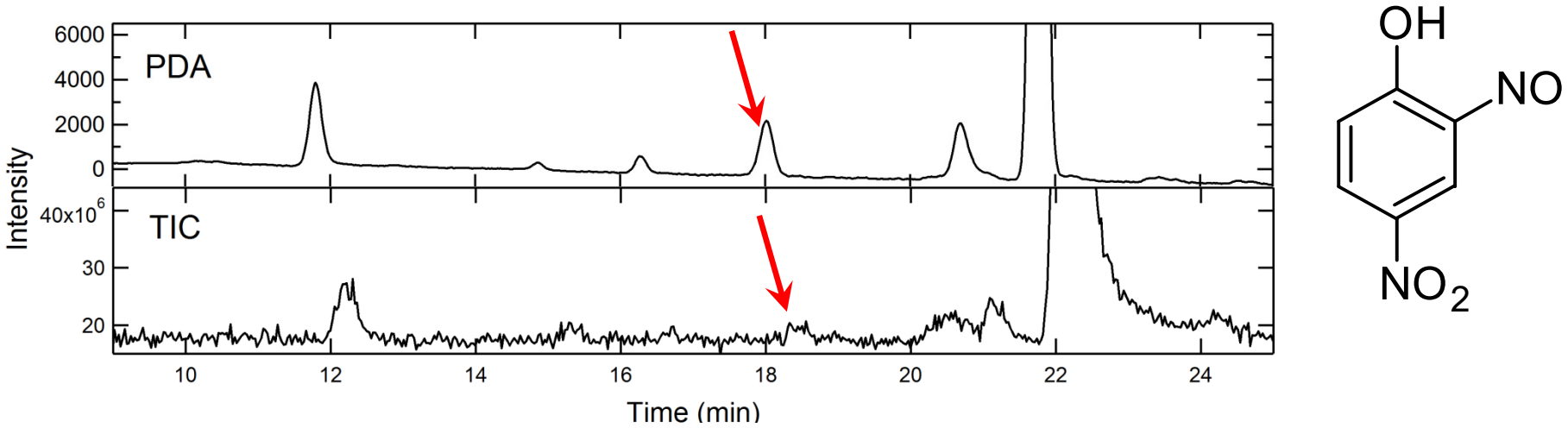
This peak (154.014590) correlates well with this the product. It corresponds to $C_6H_4NO_4^-$, an isomer of already observed compound (see Figure 10)

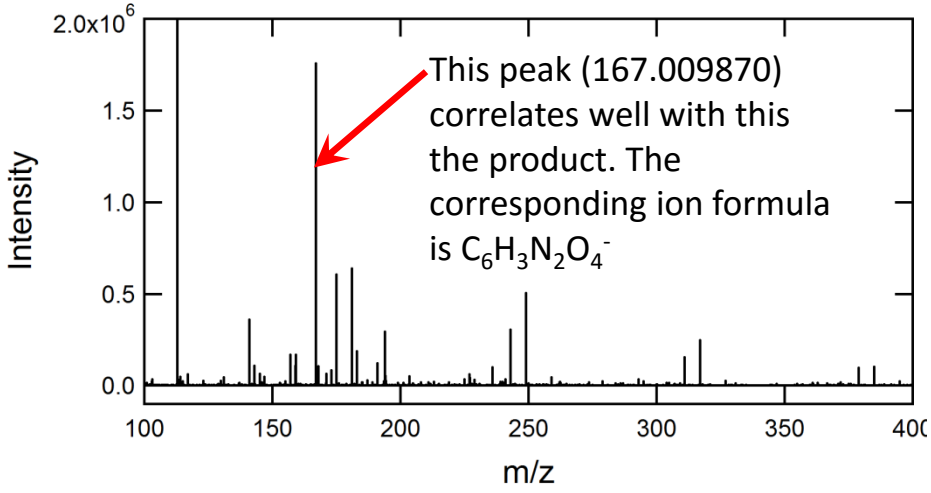
Peak Report for m/z = 154.014590 +/-3.0 ppm
C6 H4 N1 O4 m/z = 154.014581 +0.1 ppm DBE = 6.0

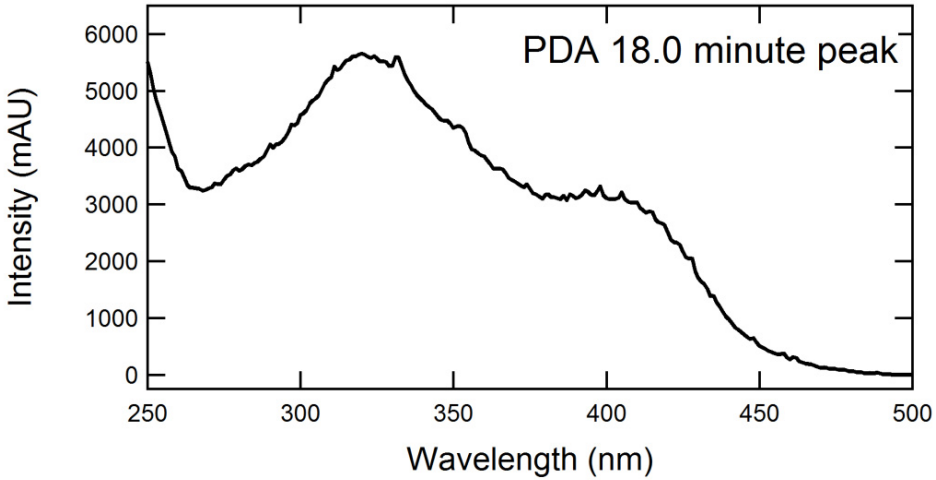
Figure S12

18.0 min peak: chromatagrams, mass spectrum, and absorption spectrum

The 18.0 min peak in the PDA chromatogram correlates to the 18.4 min peak in the MS chromatogram







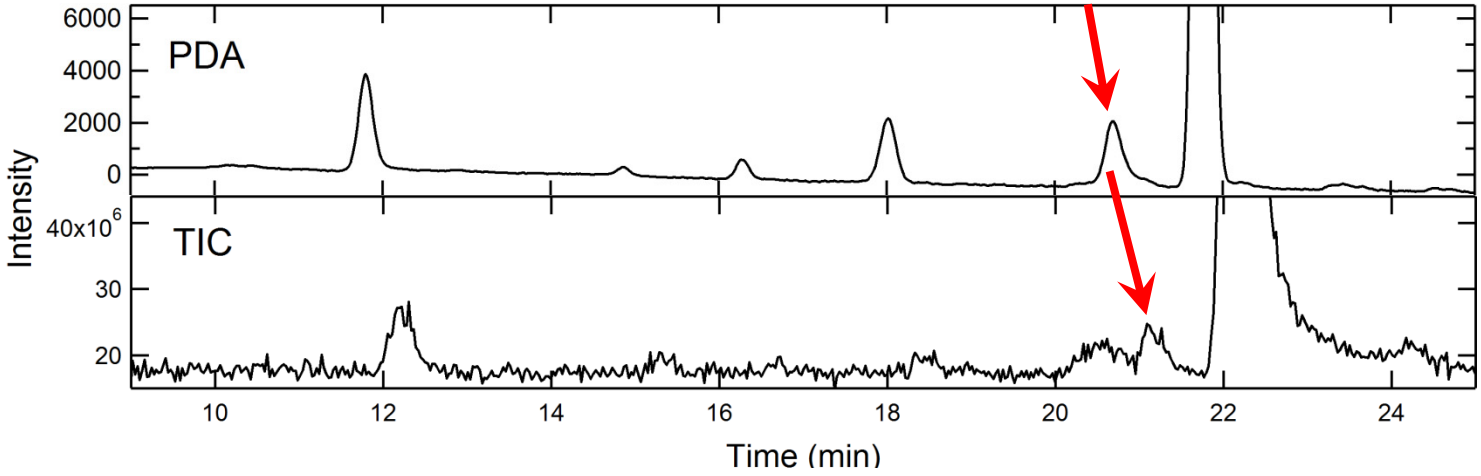
Peak Report for m/z = 167.009870 +/-2.0 ppm

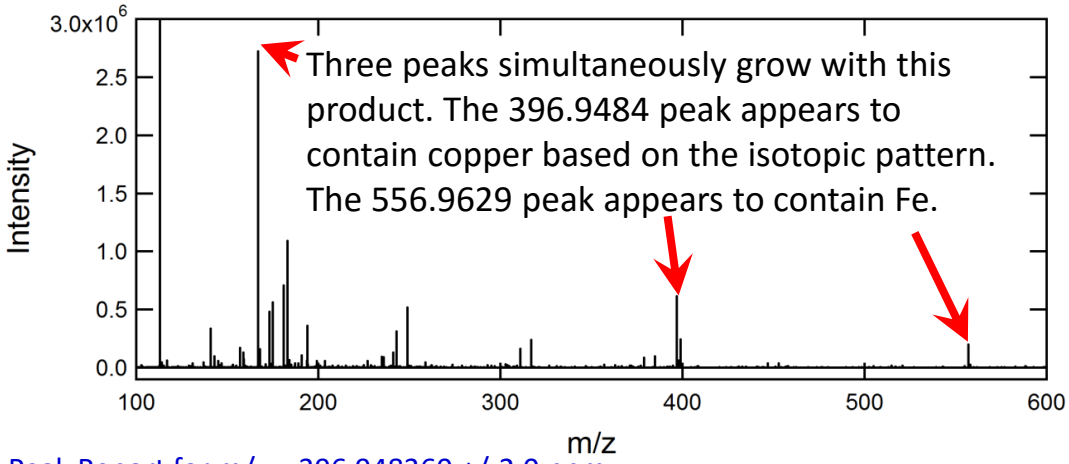
C6 H3 N2 O4 m/z = 167.009830 +0.2 ppm DBE = 7.0

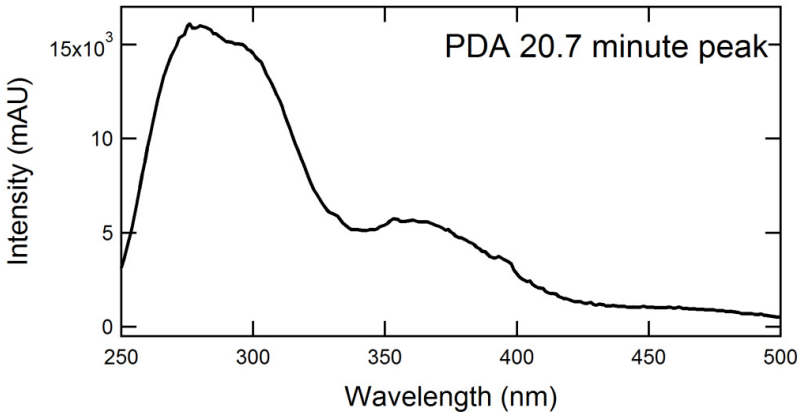
Figure S13

20.7 min peak: chromatagrams, mass spectrum, and absorption spectrum

The 20.7 min peak in the PDA chromatogram correlates to the 21.2 min peak in the MS chromatogram







Peak Report for m/z = 396.948360 +/-2.0 ppm

C12 H6 N4 O8 Cu1 m/z = 396.948709 -0.9 ppm DBE = 12.0

Peak Report for m/z = 556.962890 +/-1.0 ppm

C31 H1 N8 O1 Fe1 m/z = 556.962818 +0.1 ppm DBE = 36.0

C26 H5 O15 m/z = 556.963393 -0.9 ppm DBE = 25.0

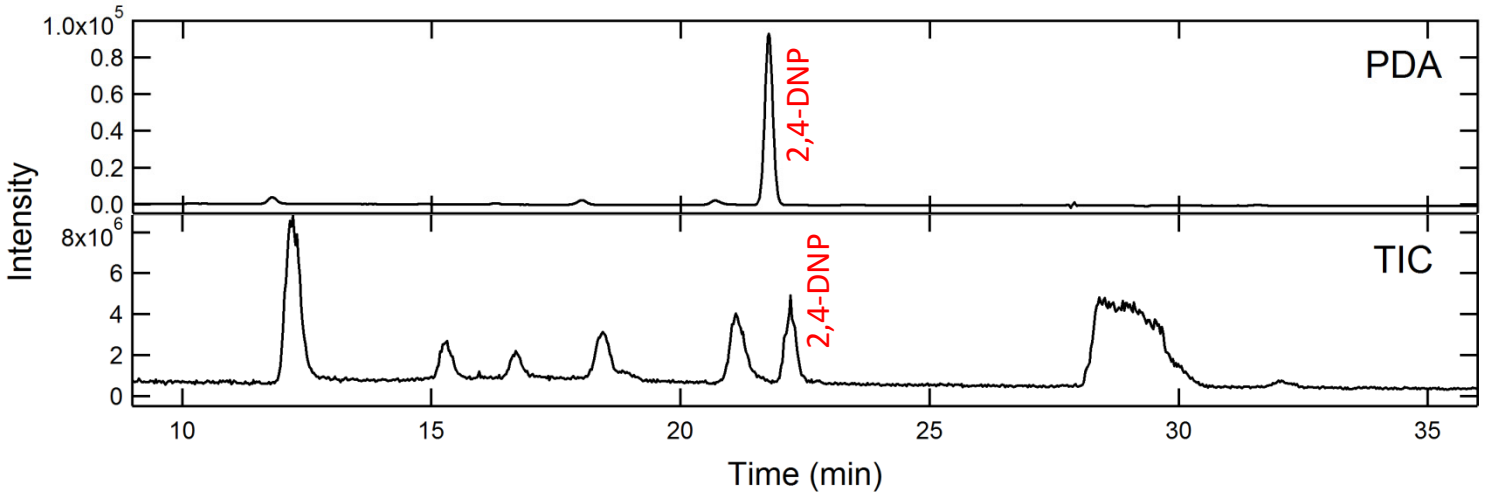
C18 H9 N6 O12 Fe1 m/z = 556.963331 -0.8 ppm DBE = 18.0

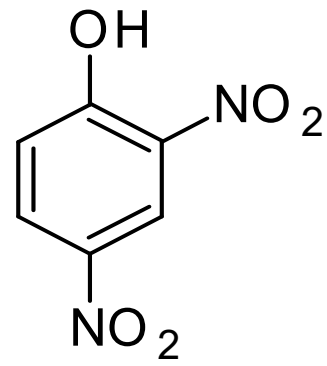
C10 H5 N8 O20 m/z = 556.962558 +0.6 ppm DBE = 13.0

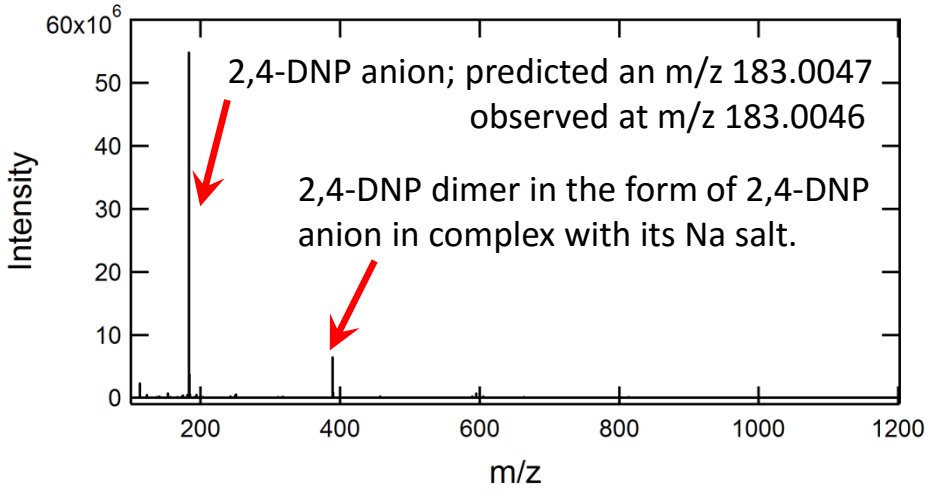
C2 H9 N14 O17 Fe1 m/z = 556.962496 +0.7 ppm DBE = 6.0

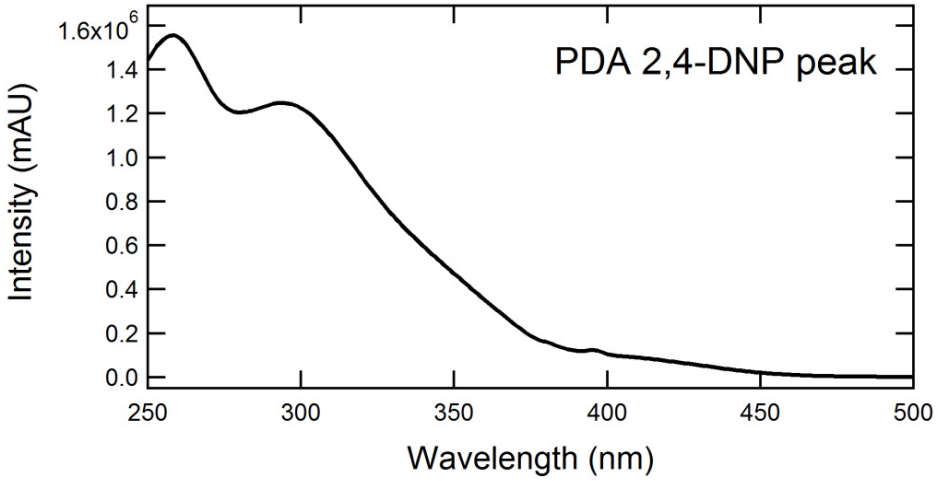
Figure S14

2,4-DNP: chromatagrams, mass spectrum, and absorption spectrum









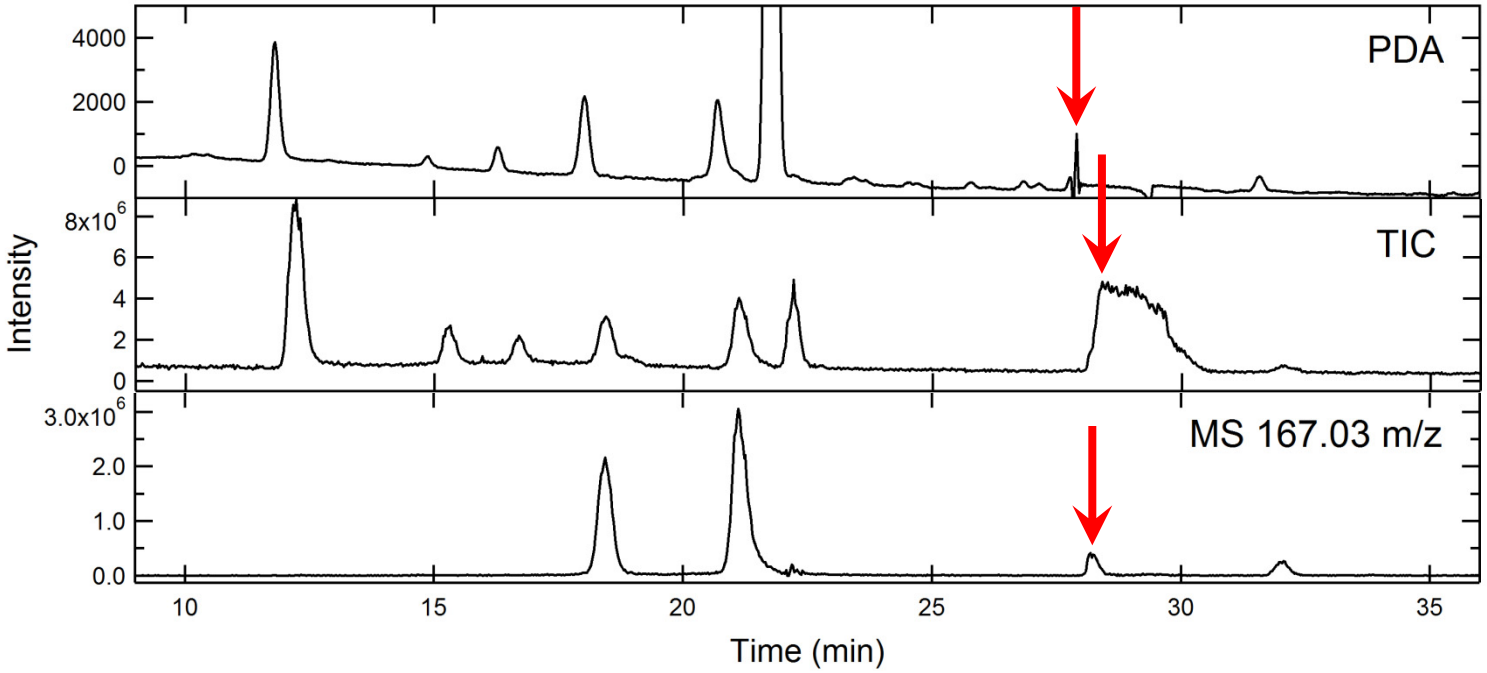
Peak Report for m/z = 183.004600 +/-2.0 ppm
C6 H3 N2 O5 m/z = 183.004745 -0.8 ppm DBE = 7.0

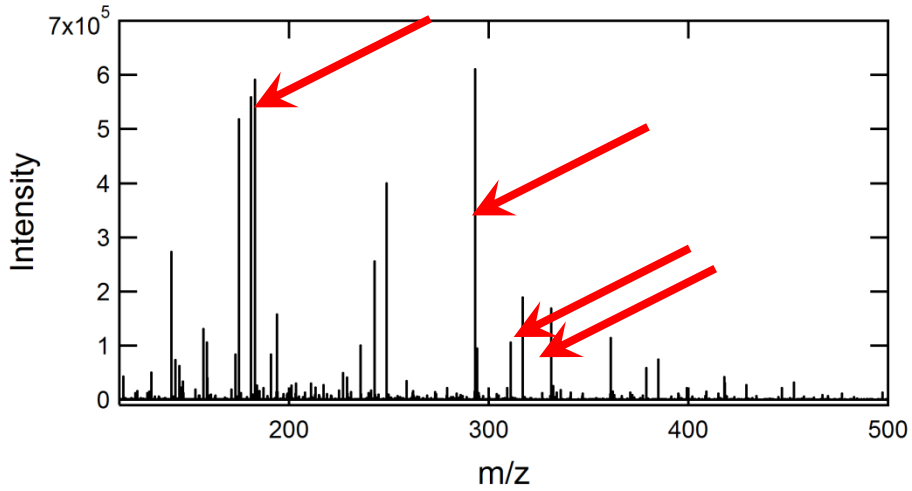
Peak Report for m/z = 388.998300 +/-2.0 ppm
C12 H6 N4 O10 Na1 m/z = 388.998710 -1.1 ppm DBE = 12.0
C10 H1 N10 O8 m/z = 388.998431 -0.3 ppm DBE = 16.0

Figure S15

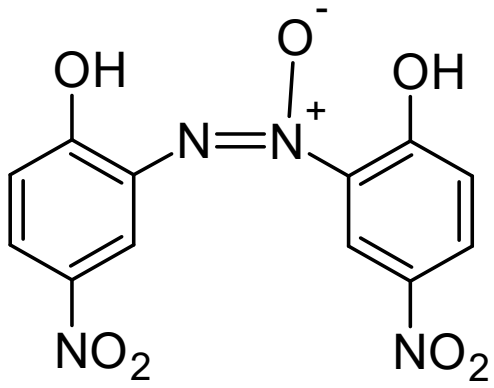
27.9 min peak: chromatagrams, mass spectrum, and absorption spectrum

The 27.9 min peak in the PDA chromatogram correlates to the 28.2 min peak in the MS chromatogram





Four peaks grow around this retention time but not quite at the same time. There might be several compounds co-eluting. One of them at 319.0321 is $C_{12}H_7N_4O_7^-$. The other is 24-DNP. We could not assign the rest.



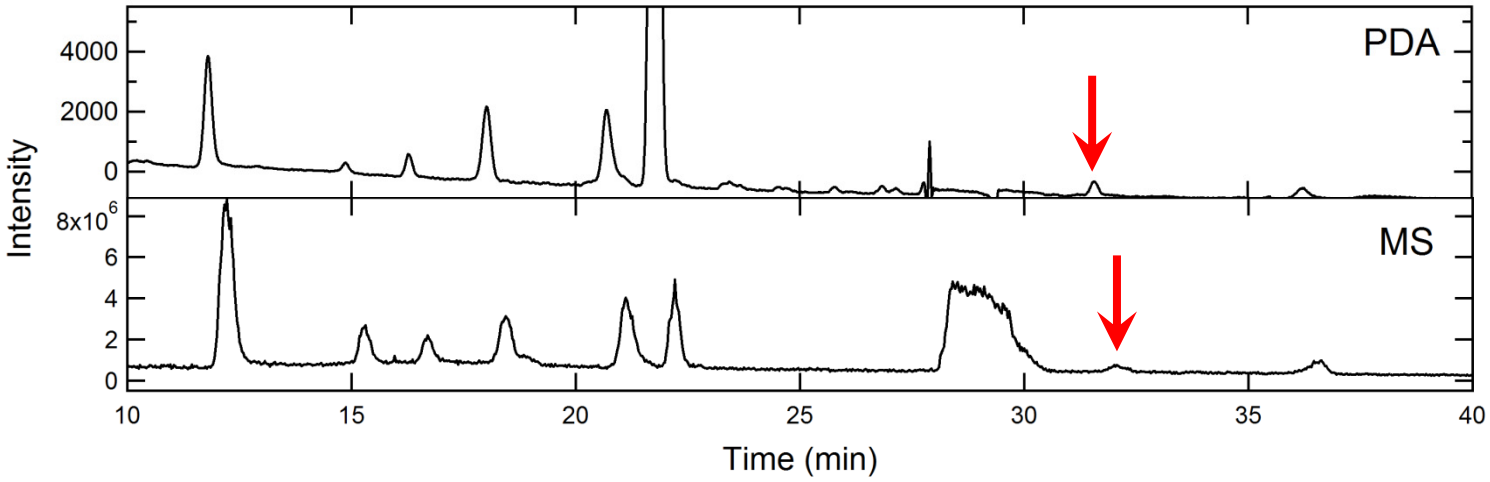
Peak Report for m/z = 319.031900 +/-2.0 ppm

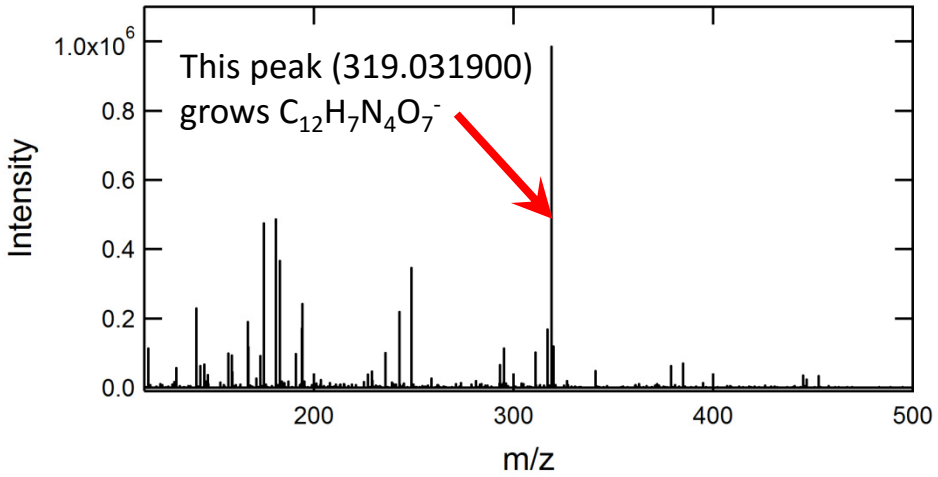
C12 H7 N4 O7 m/z = 319.032022 -0.4 ppm DBE = 12.0

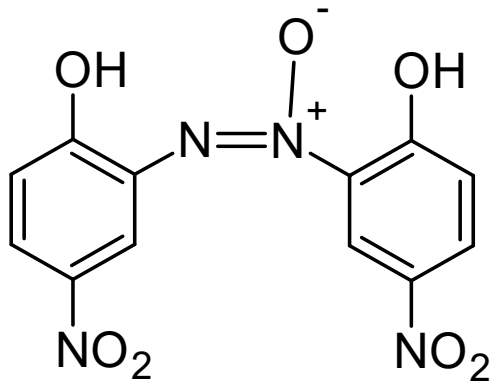
Figure S16

31.6 min peak: chromatagrams, mass spectrum, and absorption spectrum

The 31.6 min peak in the PDA chromatogram correlates to the 32.1 min peak in the MS chromatogram







Peak Report for m/z = 319.031900 +/-2.0 ppm
C12 H7 N4 O7 m/z = 319.032022 -0.4 ppm DBE = 12.0

Figure S17

Summary Table for All of the Compounds Detected in LC-PDA-MS Experiments

Retention time (min) in PDA	Retention time (min) in MS	Description of absorption spectrum observed by PDA	Major *m/z* values (negative ions) correlating with the eluted peak	Formula (neutral compound except for compounds in red which are ions)	Assignment comments
-	7.8	-	138.0197	$C_6H_5O_3N$	Loss of $-NO_2$ very small peak
11.8	12.2	280-460 nm broad spectrum	153.03055	$C_6H_6O_3N_2$	Conversion of $-NO_2$ to $-NH_2$
14.9	15.3	320 nm broad spectrum	154.0146	$C_6H_5O_4N$	Conversion of $-NO_2$ to –OH
16.3	16.7	270 nm peak	154.01459	$C_6H_5O_4N$	Conversion of $-NO_2$ to –OH
18	18.4	260-440 nm broad spectrum	167.00987	$C_6H_4O_4N_2$	Conversion of $-NO_2$ to –NO
-	19.0	-	138.0197	$C_6H_5O_3N$	Loss of $-NO_2$ very small peak
20.7	21.2	260-440 nm broad spectrum	167.00987 183.0047 396.94836 556.96289	$C_6H_4O_4N_2$ $C_6H_4O_5N_2$ Ion $C_{12}H_6N_4O_8Cu^-$ Ion $C_{18}H_9N_6O_{12}Fe^-$	The first two peaks are from a nitroso compound and 2,4-DNP. The other two are likely impurities in ESI due to metals .
21.8	22.2	2,4-DNP; absorbing where it should	183.0046 388.9989	$C_6H_4O_5N_2$ Ion $C_{12}H_6O_{10}N_4Na^-$	2,4-DNP [Na salt of 2,4-DNP] complexed to 2,4-DNP$^-$
27.9	28.2	An impurity absorbing at 280 nm	Several masses; one of them is 319.0319		
32.6	32.1	-	319.0319	$C_{12}H_8N_4O_7$	This is not a weakly-bound dimer; it is a proper ion