

Poster Reprint

ASMS 2023
Poster number TP 730

Analysis of DNPH-derivatized Aldehydes and Ketones using Agilent iQ Single Quadrupole LCMS

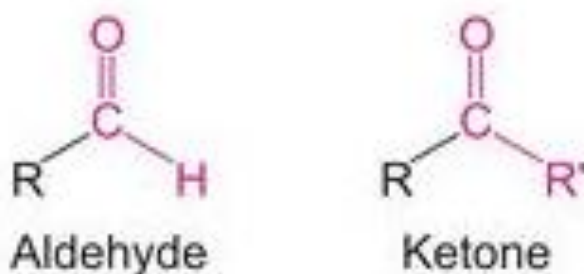
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Introduction



Aldehydes and ketones are important compounds in the chemical industry. However, these compounds can be hazardous when released into the environment. Many chemical plants, industrial hygienists and air monitoring agencies perform quantitative analysis on air samples.

Typically, this analysis is done by HPLC with UV detection since the compounds have excellent chromophores after derivatization. The typical UV wavelength being 310 nm. This method works extremely well for standards. When an unknown peak appears in a chromatogram, that peak needs to be identified as a hazardous or non-hazardous compound. Also, if a contaminant does not have an absorbance at UV wavelength 310, it may go undetected.

Therefore, this set of experiments, will be able used to lower the Limit of Detection (LOD) and Limit of Quantitation (LOQ) and detect interferences and unidentified peaks in real world samples.



Experimental

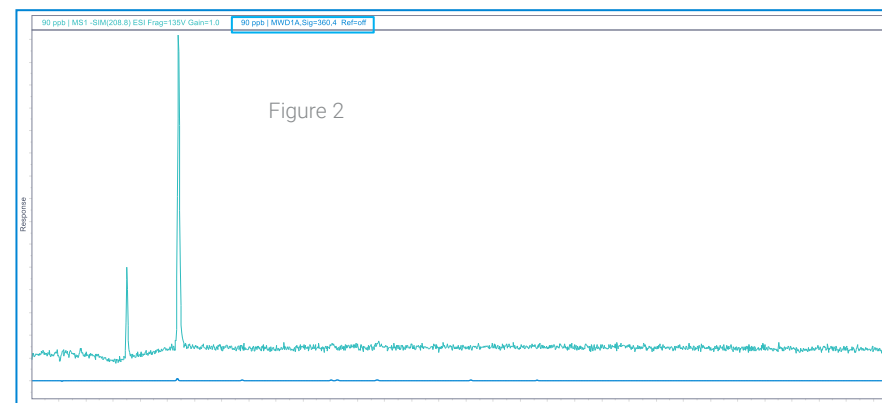
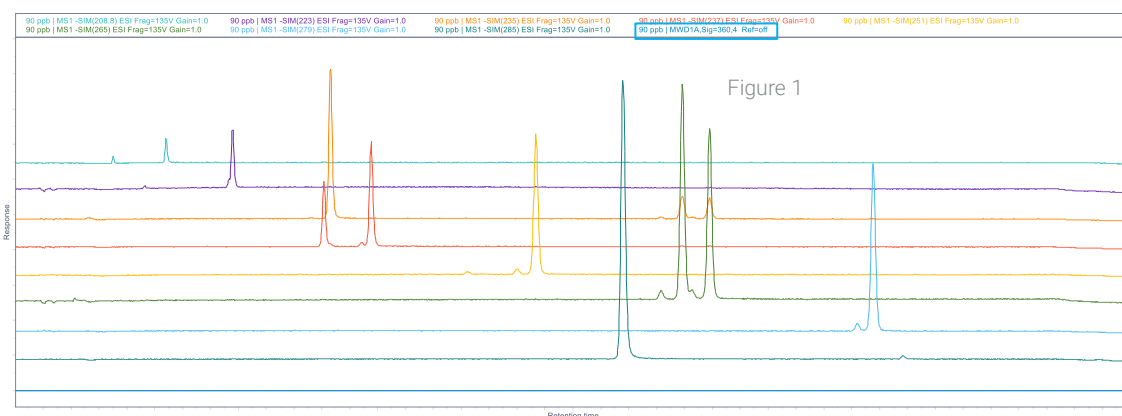
In this set of experiments, we ran 3 replicates of standard, T011/IP-6A Aldehyde/Ketone-DNPH Mix from 1 ppb to 1000 ppb to create large calibration curves. The chromatography removed the acetone for the solvent Acetonitrile/Methanol and added formic acid to add ionization. We also were given an air filter sample cartridge. This cartridge was extracted with pure Acetonitrile and run on a C18 column. A diode array detector was run in series with the LCMS. Standards and samples were run with both SIM and Scan mode. We were able to create a library with known compounds of interference. We were able to both identify interfering compounds, and to quantitate in the same analytical run.

Parameter	Settings																																				
Analytical Column	Agilent Poroshell EC C18, 3.0 x 150mm, 1.9 μ m Part Number 693675-302																																				
Column Temperature	30.0° C																																				
Injection Volume	0.5 μ L																																				
Run Time	40.00 minutes																																				
Post-run Time	5.00 minutes																																				
Flow Rate	0.50 mL/minute																																				
Mobile Phase A	Water																																				
Mobile Phase B	Acetonitrile																																				
Mobile Phase C	Methanol																																				
Mobile Phase D	0.1% Formic Acid in Water																																				
Quaternary Pump Gradient	<table border="1"> <thead> <tr> <th>Time (min)</th> <th>Flow (mL/min)</th> <th>%A</th> <th>%B</th> <th>%C</th> <th>%D</th> </tr> </thead> <tbody> <tr> <td>0.00</td> <td>0.50</td> <td>50.00</td> <td>22.50</td> <td>22.50</td> <td>5.00</td> </tr> <tr> <td>14.50</td> <td>0.50</td> <td>42.00</td> <td>26.50</td> <td>26.50</td> <td>5.00</td> </tr> <tr> <td>30.50</td> <td>0.50</td> <td>28.00</td> <td>33.50</td> <td>33.50</td> <td>5.00</td> </tr> <tr> <td>34.50</td> <td>0.50</td> <td>28.00</td> <td>33.50</td> <td>33.50</td> <td>5.00</td> </tr> <tr> <td>36.00</td> <td>0.50</td> <td>00.00</td> <td>45.00</td> <td>45.00</td> <td>5.00</td> </tr> </tbody> </table>	Time (min)	Flow (mL/min)	%A	%B	%C	%D	0.00	0.50	50.00	22.50	22.50	5.00	14.50	0.50	42.00	26.50	26.50	5.00	30.50	0.50	28.00	33.50	33.50	5.00	34.50	0.50	28.00	33.50	33.50	5.00	36.00	0.50	00.00	45.00	45.00	5.00
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36.00	0.50	00.00	45.00	45.00	5.00																																
UV Wavelength (nm)	360																																				
MS Ion Source	Electrospray																																				
MS Mode	Auto Acquire (Negative)																																				
Scan Type	Scan and Single Ion Monitoring (SIM)																																				

*This run time is significantly reduced if you do not need DAD data. In this poster we needed to compare UV to MSD results.

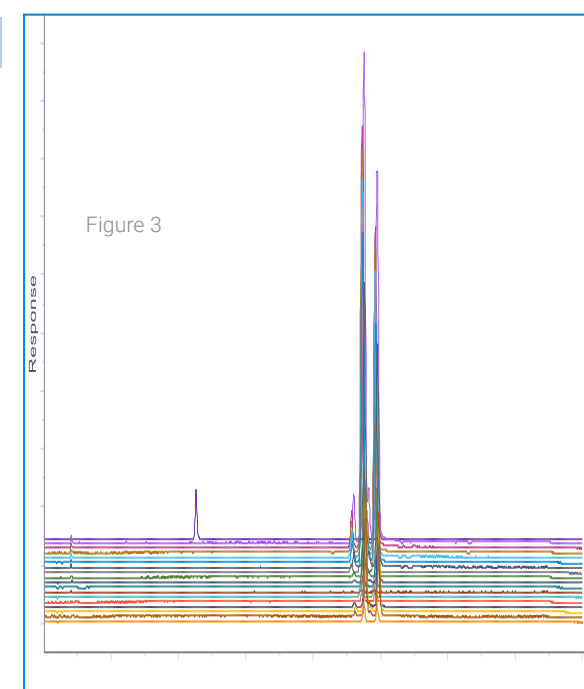
LOD and LOQ Comparison with Traditional UV Method

Compound	m/z	LOD MS (ppb)	LOQ MS (ppb)	LOQ UV (ppb)
Acetaldehyde-2,4-dinitrophenylhydrazone	223	3	6	45
Acetone-2,4-dinitrophenylhydrazone	227	1.05	1.5	45
Acrolein-2,4-dinitrophenylhydrazone	235	1.05	1.5	45
Benzaldehyde-2,4-dinitrophenylhydrazone	285	0.75	3	90
Butyraldehyde-2,4-dinitrophenylhydrazone	251	0.9	4.5	75
Crotonaldehyde-2,4-dinitrophenylhydrazone	249	6	9	90
2,5-Dimethylbenzaldehyde 2,4-dinitrophenylhydrazone	313	3	6	90
Formaldehyde-2,4-dinitrophenylhydrazone	208.8	4.5	9	12
Hexaldehyde-2,4-dinitrophenylhydrazone	279	0.75	4.5	90
Isovaleraldehyde 2,4-dinitrophenylhydrazone	265	0.9	3	75
Propionaldehyde-2,4-dinitrophenylhydrazone	237	1.05	4.5	60
o-Tolualdehyde 2,4-dinitrophenylhydrazone	299	1.05	4.5	90
m-Tolualdehyde 2,4-dinitrophenylhydrazone	299	1.05	4.5	90
p-Tolualdehyde 2,4-dinitrophenylhydrazone	299	1.05	4.5	90
Valeraldehyde-2,4-dinitrophenylhydrazone	265	0.75	1.5	75



The highest LOQ value of the LCMS data, 9 ppb, is an order of magnitude larger than the level of concentration where all the peaks in the UV can be seen (90 ppb). Figure 1 shows an overlay of the UV chromatogram the darker blue chromatogram on the bottom at 90 ppb with the SIMS. The LCMS gives significantly more response. Figure 2 shows an overlay of the UV chromatogram and the SIM 208 in the same scale. Formaldehyde, which has the lowest LOQ, is still significantly lower in magnitude.

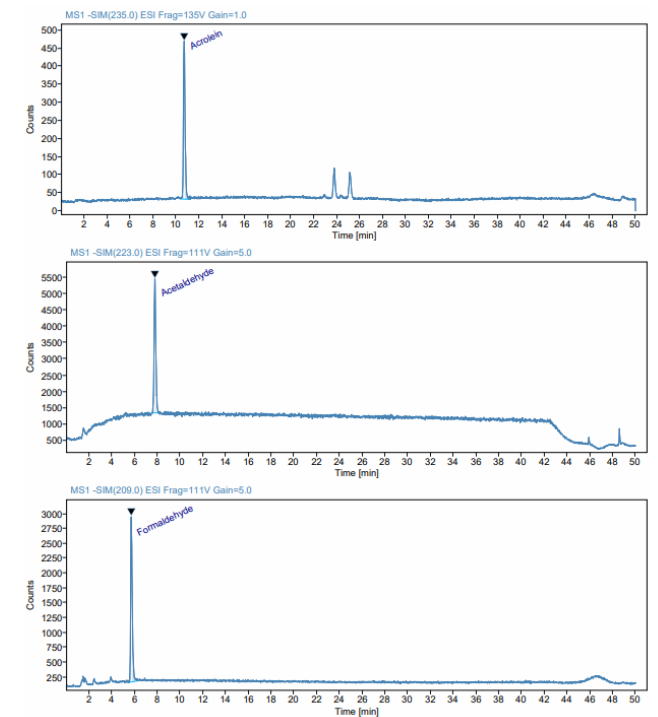
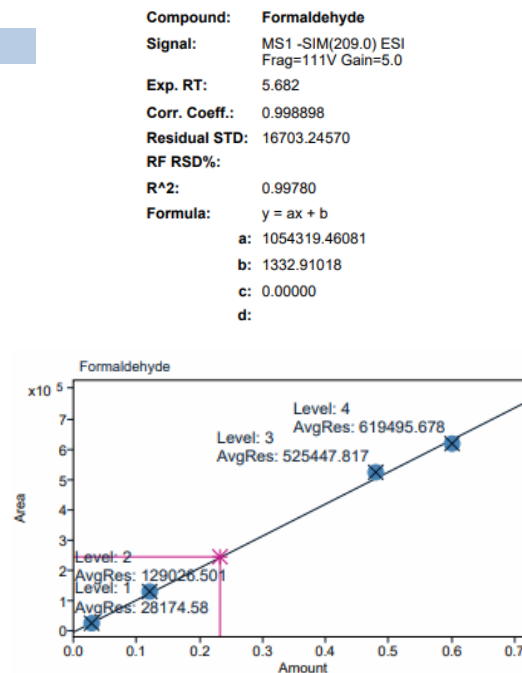
Compound	m/z	Linearity
Acetaldehyde-2,4-dinitrophenylhydrazone	223	0.999
Acetone-2,4-dinitrophenylhydrazone	227	0.999
Acrolein-2,4-dinitrophenylhydrazone	235	0.999
Benzaldehyde-2,4-dinitrophenylhydrazone	285	0.999
Butyraldehyde-2,4-dinitrophenylhydrazone	251	0.999
Crotonaldehyde-2,4-dinitrophenylhydrazone	249	0.999
2,5-Dimethylbenzaldehyde 2,4-dinitrophenylhydrazone	313	0.999
Formaldehyde-2,4-dinitrophenylhydrazone	208.8	0.999
Hexaldehyde-2,4-dinitrophenylhydrazone	279	0.999
Isovaleraldehyde 2,4-dinitrophenylhydrazone	265	0.999
Propionaldehyde-2,4-dinitrophenylhydrazone	237	0.999
o-Tolualdehyde 2,4-dinitrophenylhydrazone	299	0.999
m-Tolualdehyde 2,4-dinitrophenylhydrazone	299	0.999
p-Tolualdehyde 2,4-dinitrophenylhydrazone	299	0.999
Valeraldehyde-2,4-dinitrophenylhydrazone	265	0.75



Overlay of two close compounds at the same m/z, with 2.7 peak resolution 0.105 ppb to 1500 ppb

Spike Sample Recovery results

Compound	Accuracy
Acetaldehyde-2,4-dinitrophenylhydrazone	101.6
Acetone-2,4-dinitrophenylhydrazone	100.5
Acrolein-2,4-dinitrophenylhydrazone	101.2
Benzaldehyde-2,4-dinitrophenylhydrazone	100.9
Butyraldehyde-2,4-dinitrophenylhydrazone	101.6
Crotonaldehyde-2,4-dinitrophenylhydrazone	100.8
2,5-Dimethylbenzaldehyde 2,4-dinitrophenylhydrazone	102.4
Formaldehyde-2,4-dinitrophenylhydrazone	101.2
Hexaldehyde-2,4-dinitrophenylhydrazone	102.4
Isovaleraldehyde 2,4-dinitrophenylhydrazone	100.9
Propionaldehyde-2,4-dinitrophenylhydrazone	102.7
o-Tolualdehyde 2,4-dinitrophenylhydrazone	103.5
m-Tolualdehyde 2,4-dinitrophenylhydrazone	103.5
p-Tolualdehyde 2,4-dinitrophenylhydrazone	103.5
Valeraldehyde-2,4-dinitrophenylhydrazone	0.75

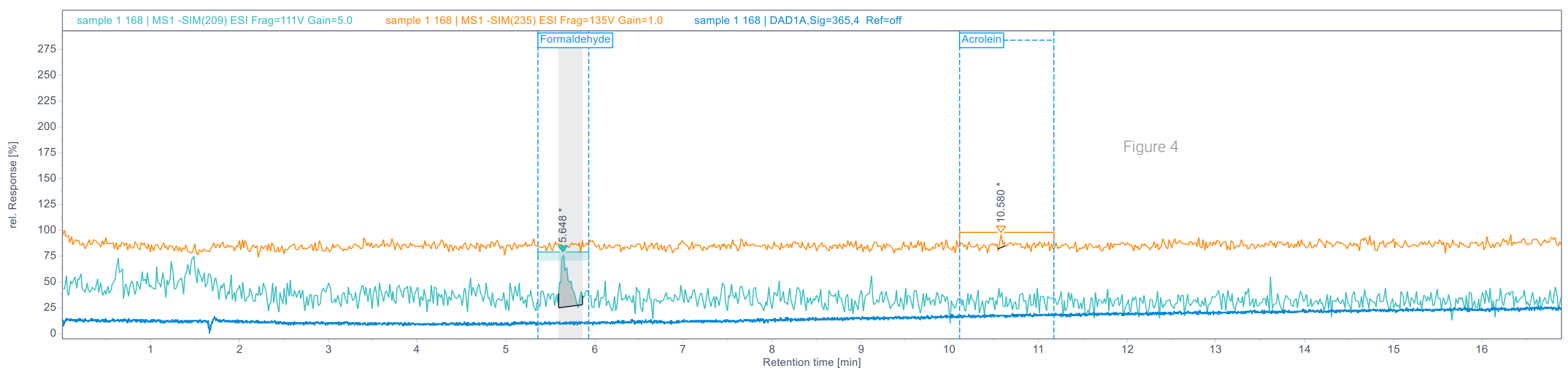


Sample Results

Figure 4 shows an overlay of the two compounds found in the sample. Note that no compounds were found in the blue (UV) chromatogram. All Chromatograms are in full scale.

Injection Results

#	Name	Signal description	RT (min)	Area (Counts-s)	Area%	Height (Counts)	Height%	Amount	Concentration	Start time (min)	End time (min)
1	Formaldehyde	MS1 -SIM(209) ESI Frag=111V Gain=5	5.648	482.398	100.000	70.558	100.00	0.645	0.645	5.594	5.867
2	Acrolein	MS1 -SIM(235) ESI Frag=135V Gain=1	10.580	34.773	100.000	17.594	100.00	0.381	0.381	10.543	10.633



Conclusions

- ✓ The LC MS methodology adds an order of magnitude sensitivity to the existing UV method. This allows for previously undetected peaks to be quantitated.
- ✓ The selectivity of the LCMS allows for faster runtimes
- ✓ The ability for library searching of known unknowns within the same run.

References

- 1 Carbonyl-DNPH Derivatives in Indoor and In-car Air by UHPL C and Triple Quadrupole LC/MS
 Rong-jie Fu, Maoxin Cao, and Ying Wang
 Agilent Technologies (Shanghai) Co. Ltd, (Agilent PN 5991-2125EN)
- 2 Anon. Determination of Carbonyl Compounds by High Performance Liquid Chromatography (HPLC),
 EPA Method 8315a. Environmental Protection Agency, Washington, DC, USA (1996).
- 3 Analysis of DNPH-derivatized Aldehydes and Ketones using the Agilent 1220 Infinity LC System with Diode Array Detector
 Sonja Schneider .
 Agilent Technologies, Inc. Waldbronn, Germany (Agilent PN 5991-1545EN)

<https://www.agilent.com/en/promotions/asms>

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