

SUPPLEMENTARY INFORMATION

On-line SPME derivatization for the sensitive determination of multi-oxygenated volatile compounds in air

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Figure SI.1 Derivatization reactions of multi-oxygenated compounds.

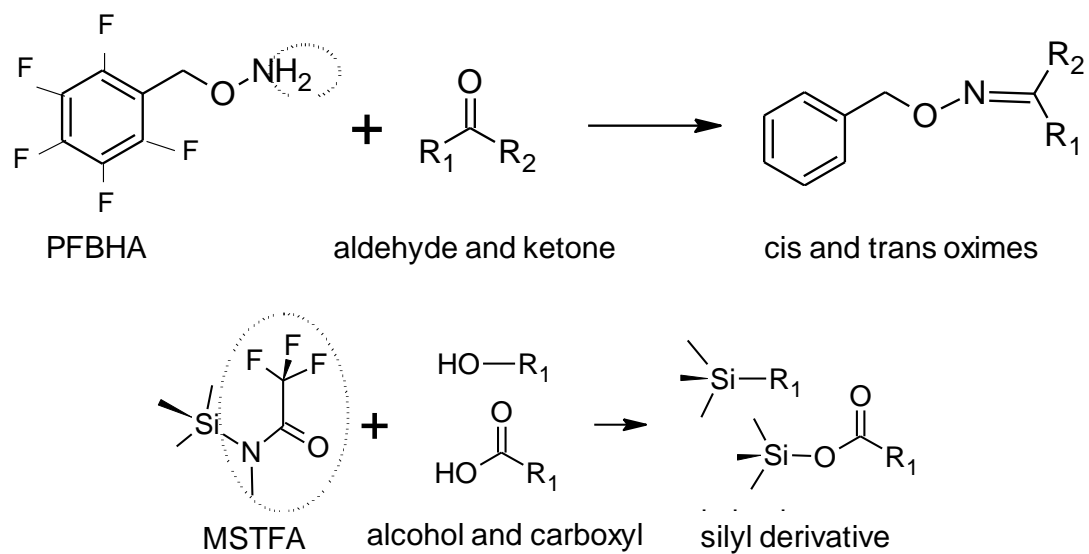


Table SI.1. A detailed description of techniques and institutions that participated in the OVOCs intercomparison of EUROCHAMP project.

Instrumentation Analysis Technique	Institute Name	ID
On-line SPME-GCMS plus derivatization	CEAM Foundation	CEAM
FTIR		
DNPH cartridges analyzed by LC-MS		
PTR-ToF-MS	Forschungszentrum Jülich	FZJ
SIFT-MS	University of York	York
PTR-ToF-MS	Leeds University	Leeds

Figure SI.2 The structures of carbonyl model compounds

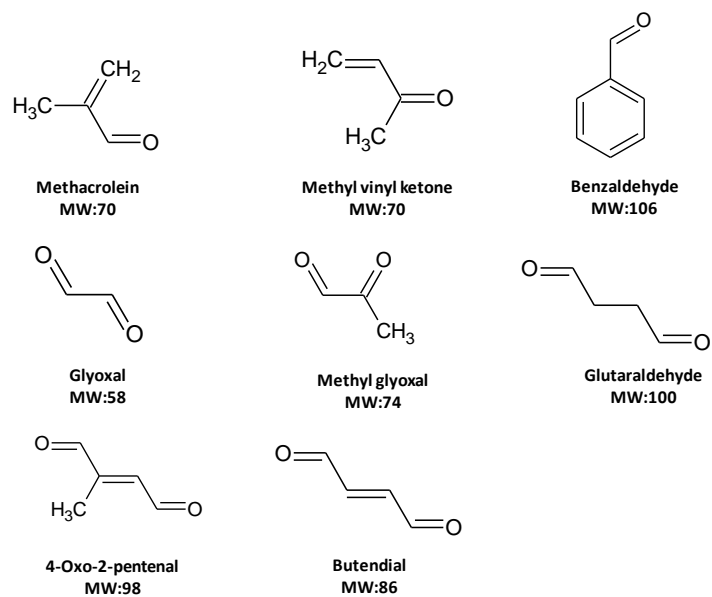
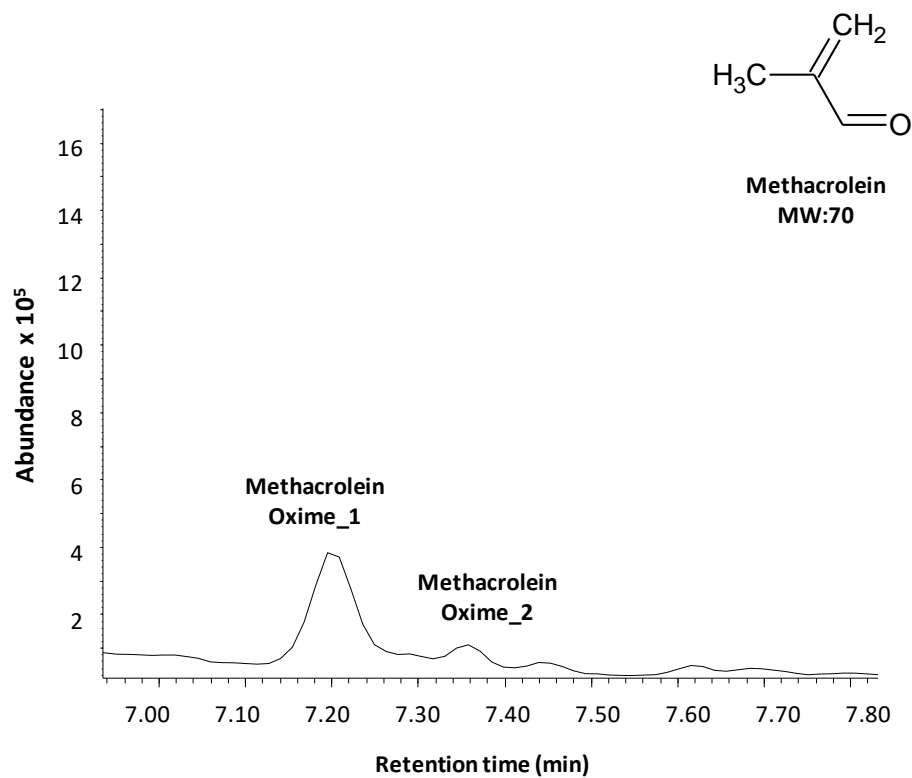
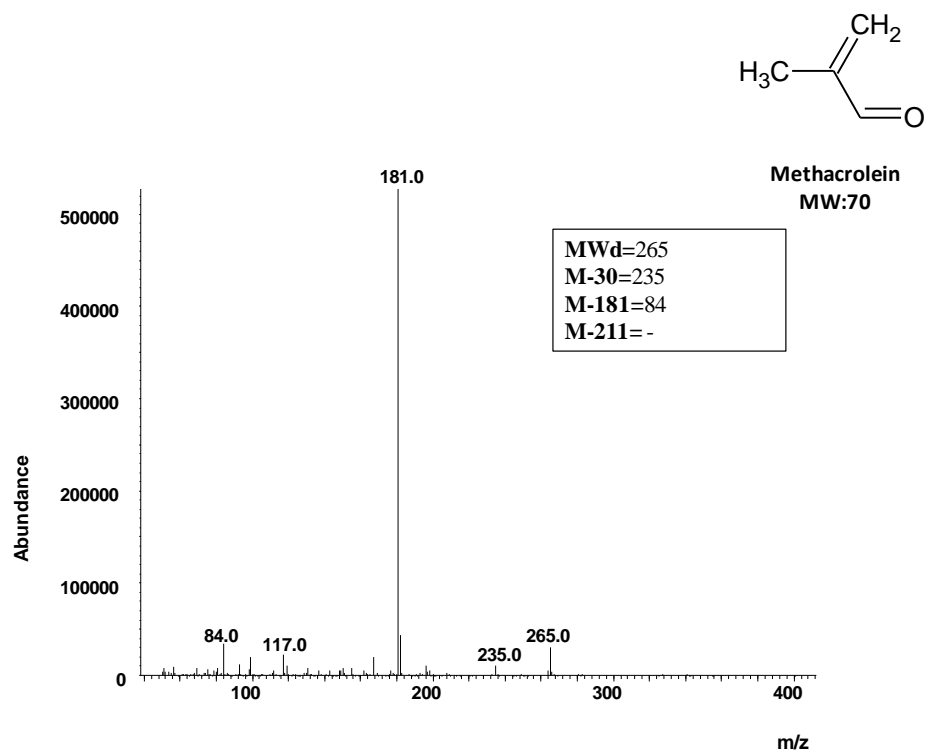


Figure SI. 3 The chromatograms of oxime peaks of each carbonyl compound and its corresponding mass spectra.

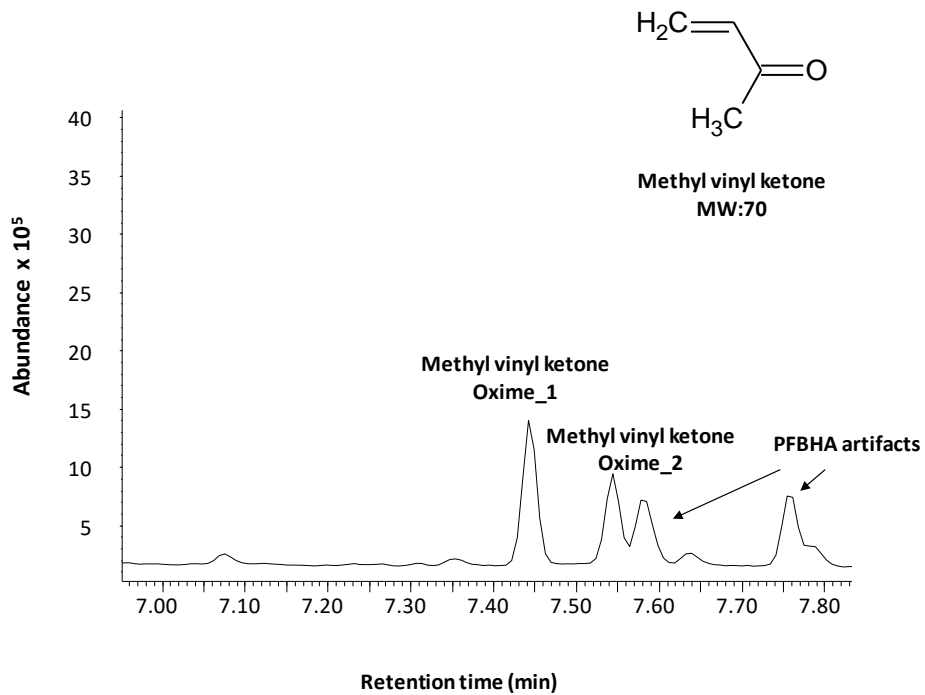
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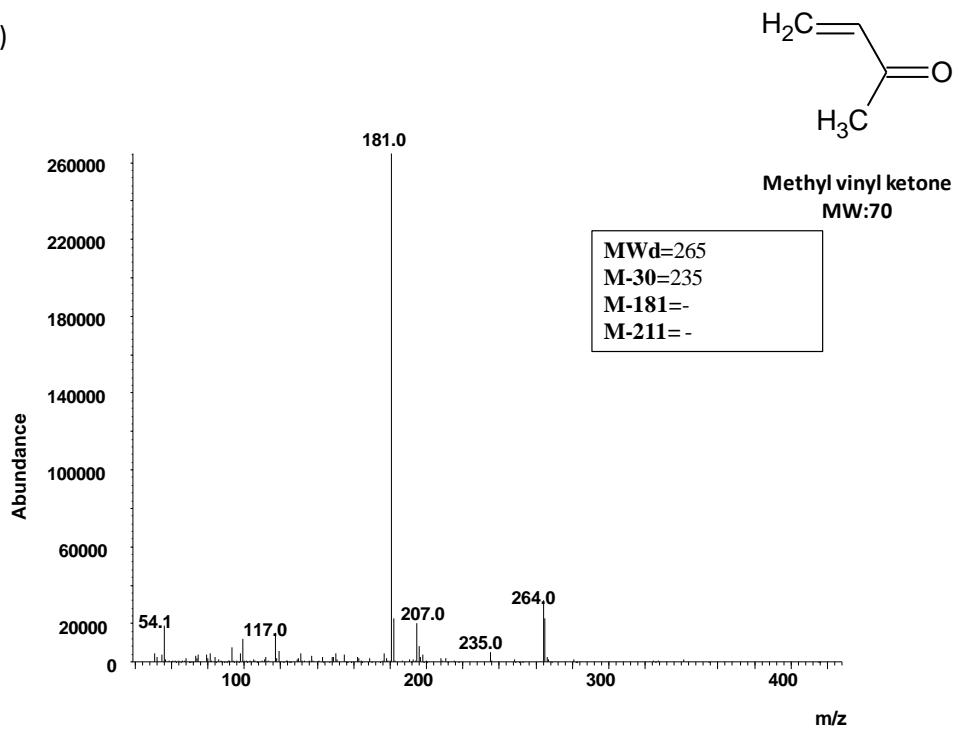
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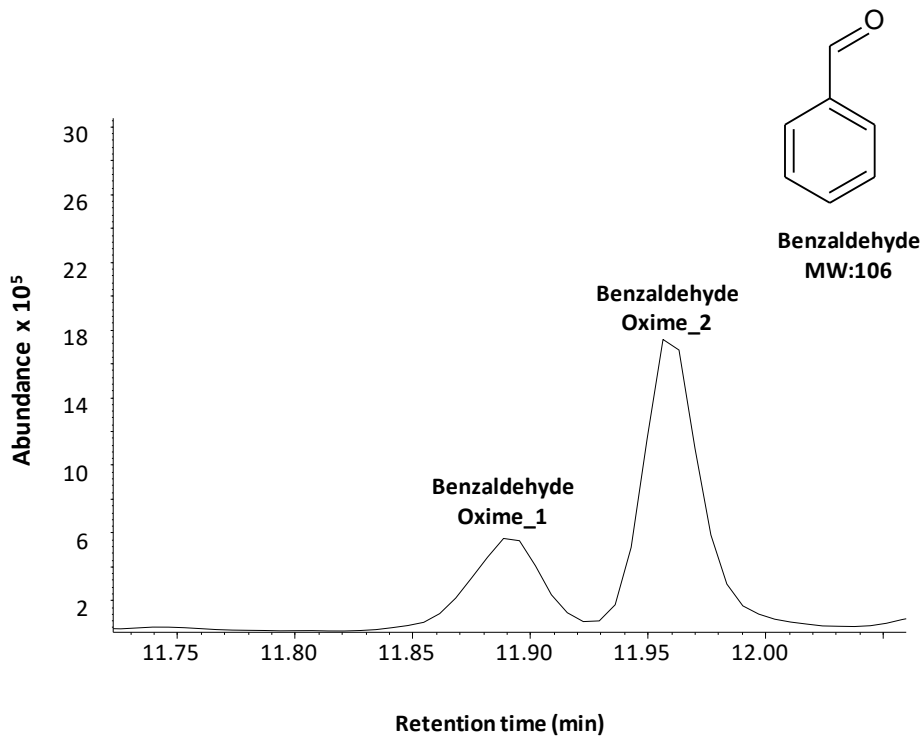
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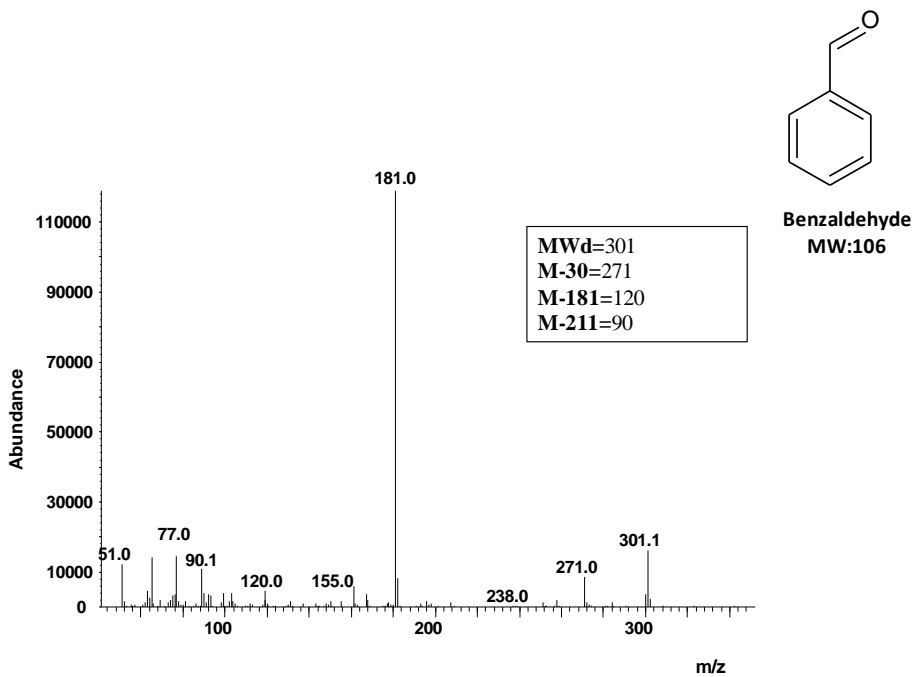
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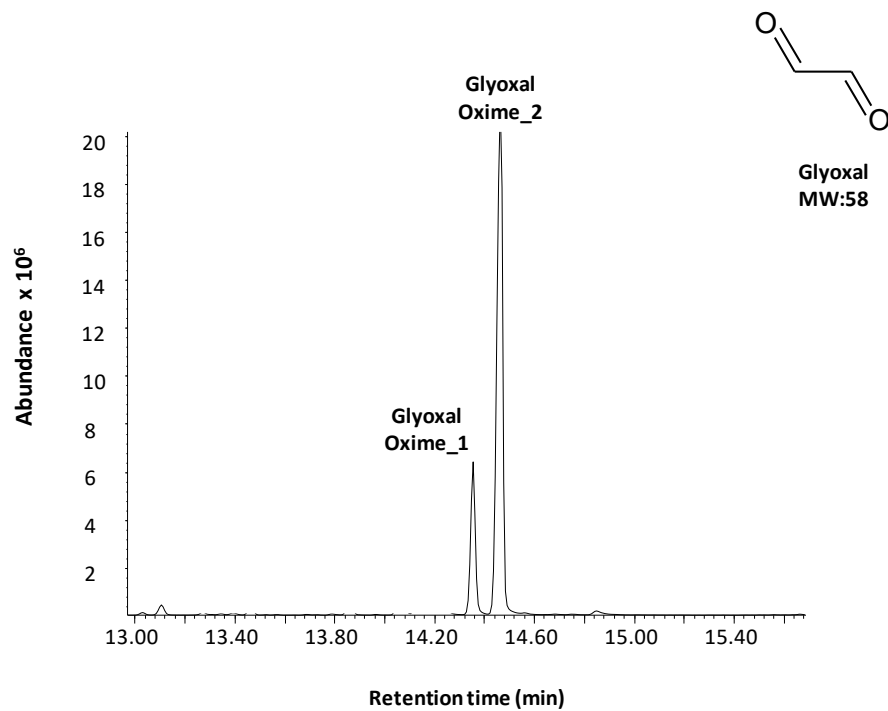
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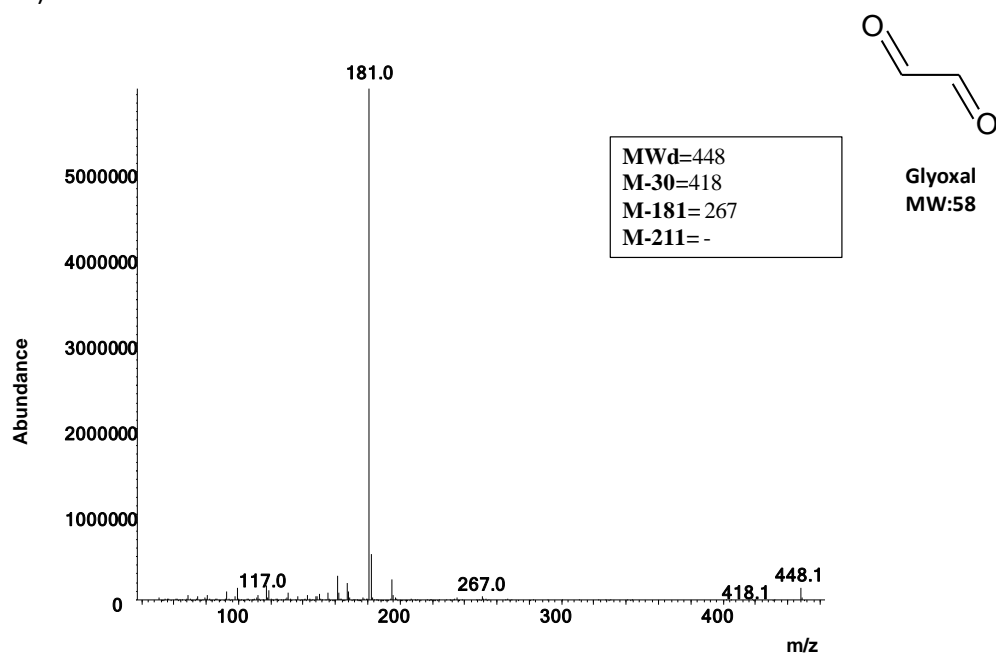
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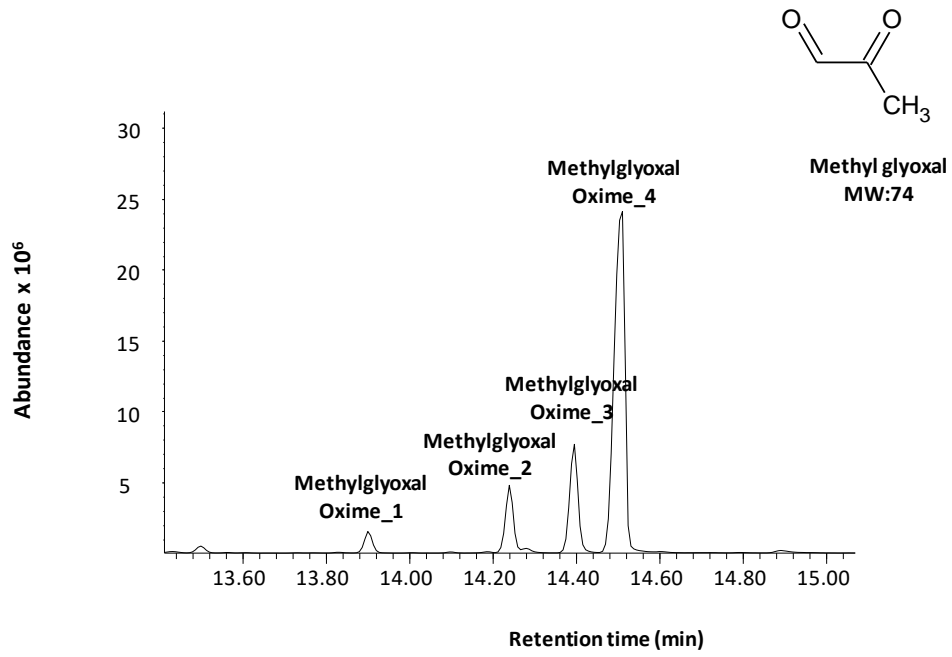
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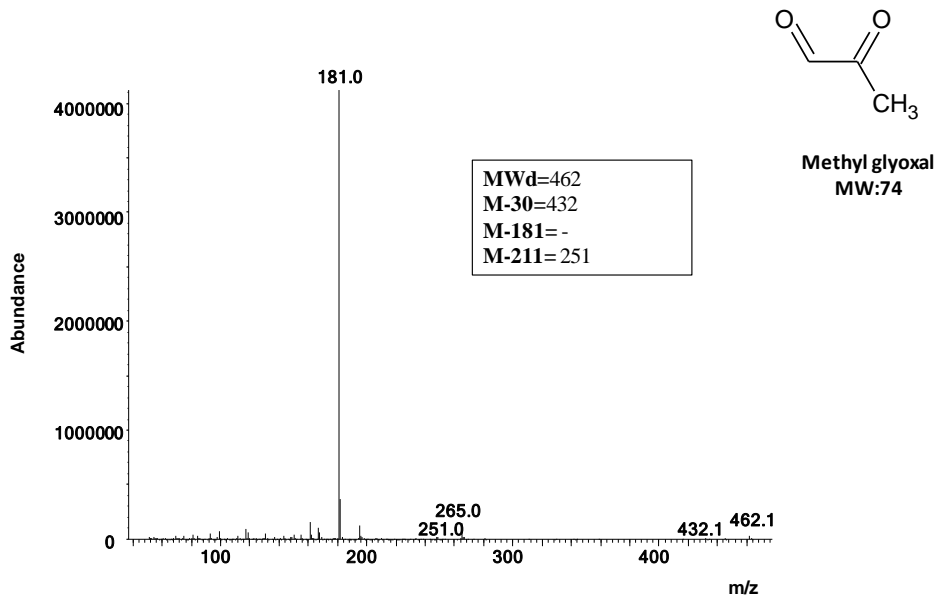
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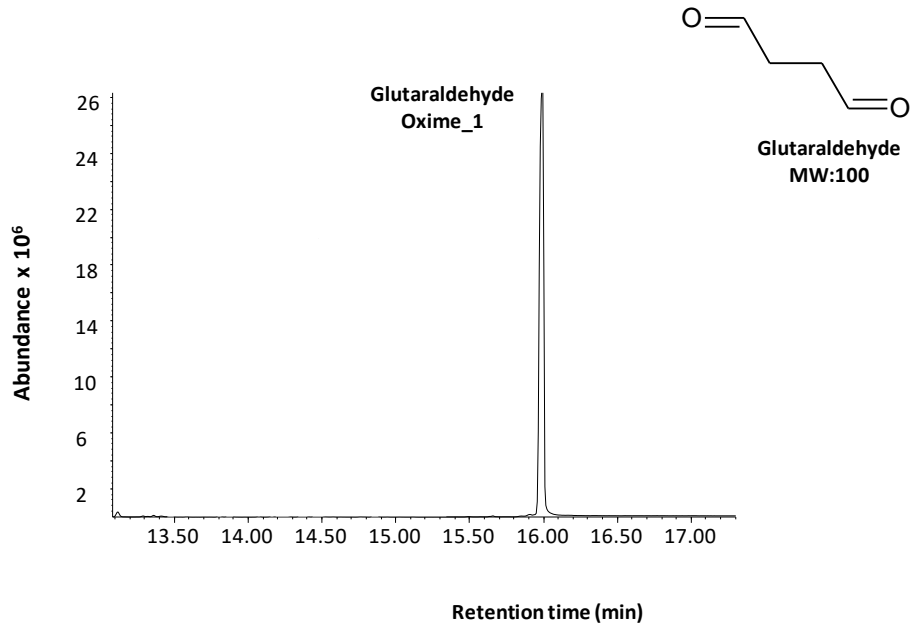
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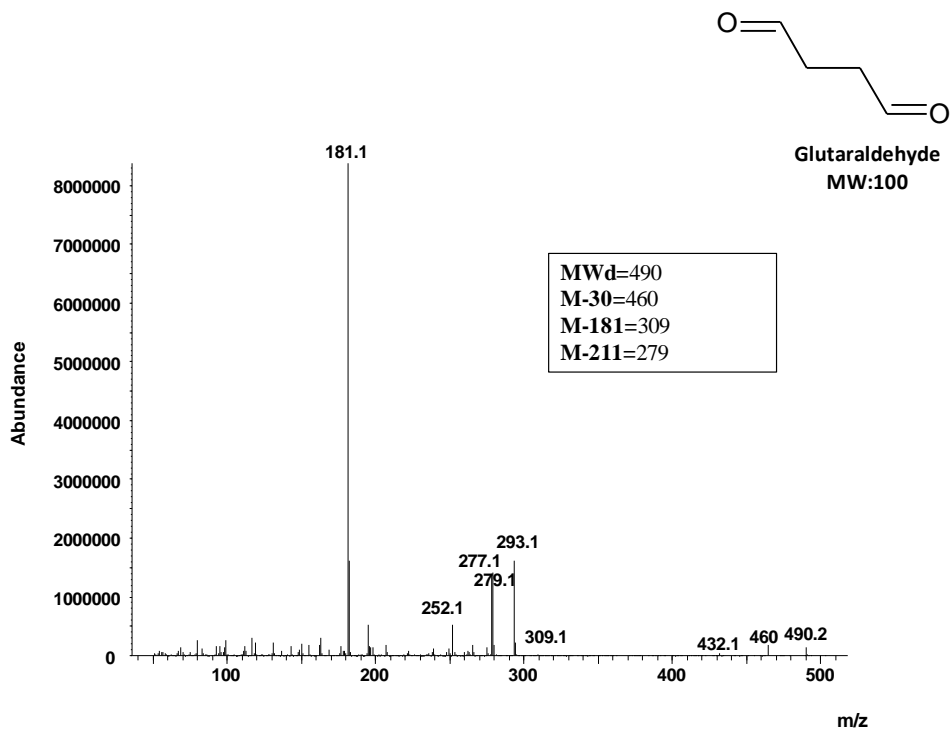
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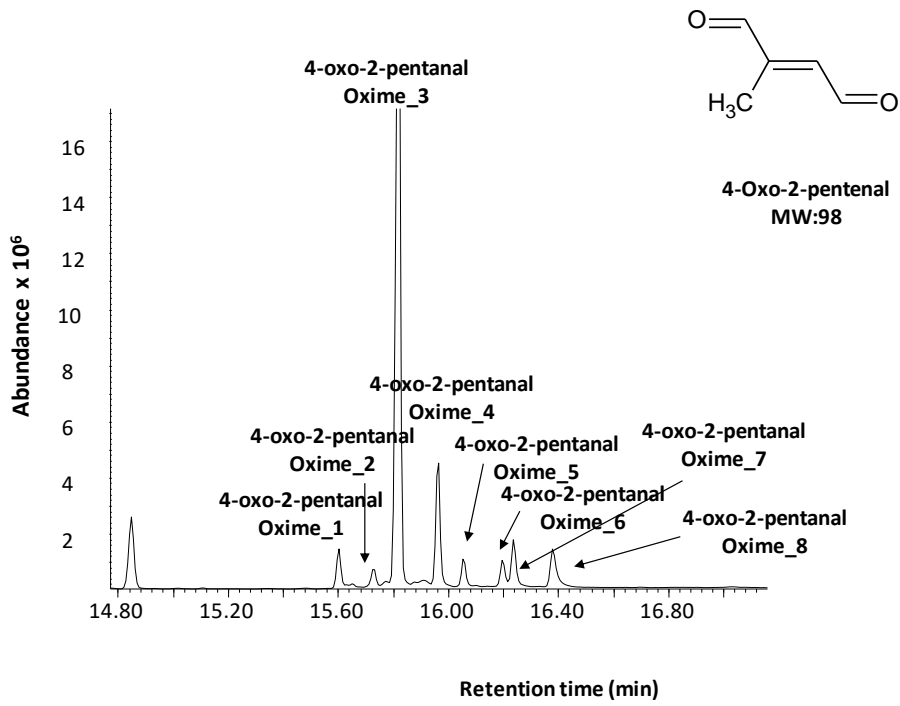
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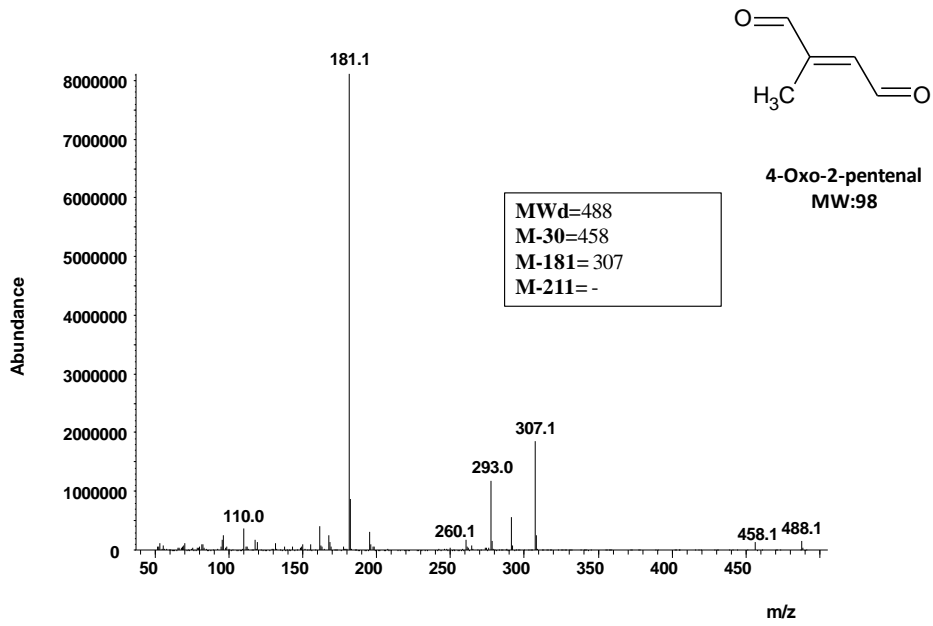
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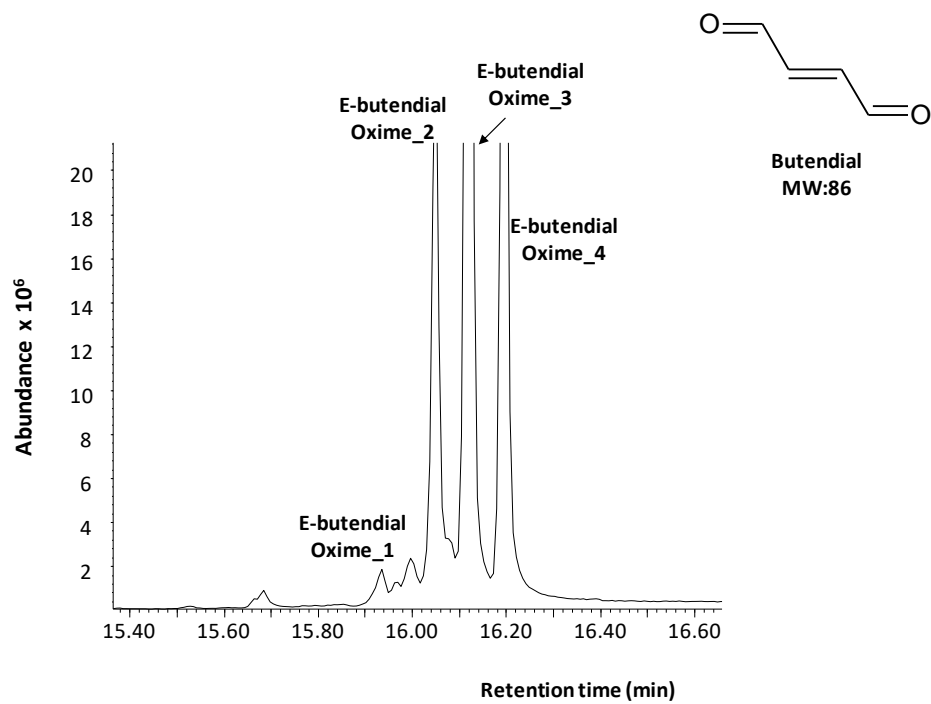
m)



n)



o)



p)

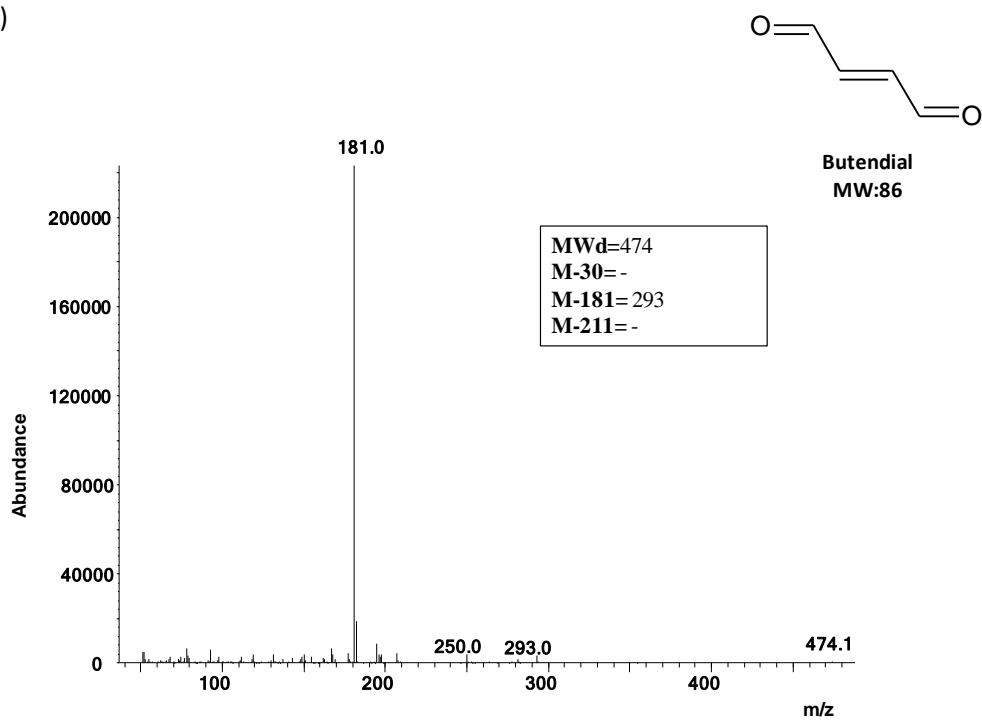


Table SI.2 The calculated recoveries of 8 OVOCs mixture.

<i>Compound</i>	<i>R.F</i>	<i>R</i> ²	<i>[]</i> _{theoretical} (ppbV)	<i>[]</i> _{experimental} (ppbV)	<i>Losses partial</i> <i>derivatization</i> (%)	<i>Recovery main</i> <i>oxime</i> (%)
Methacrolein	9027	0.982	45	44	0.0	99.0
Methyl vinyl ketone	8046	0.971	59	57	0.0	97.1
Benzaldehyde	19776	0.985	71	69	0.0	96.6
Glyoxal	427247	0.992	40	40	0.3	99.5
Methylglyoxal	4390256	0.997	45	45	0.2	99.7
E-4-oxo-2-pentenal	6273254	0.990	15	14	0.5	95.9
Glutaraldehyde	10465617	0.952	27	25	1.6	91.3
E-butenedial	4863653	0.982	10	10	0.6	99.0

R.F: response factor

Table SI. 3 Optimization experiments of on-fiber MSTFA derivatization after on-fiber PFBHA derivatization. Peaks: glycolaldehyde isomer 1 (8.2 min, MWd 327), glycolaldehyde isomer 2 (8.3 min, MWd 327), hydroxyacetone isomer 1 (9.8 min, MWd 341), hydroxyacetone isomer 2 (9.9 min, MWd 341), succinic acid (10.4 min, MWd: 262).

<i>Step</i>	<i>Variable</i>	<i>Range</i>	<i>Selected value</i>
Headspace generation	MSTFA concentration	10 – 100 μ L	40 μ L
	TMCS Catalyst	1 – 20 μ L	5 μ L
	Loading temperature	20 – 50 $^{\circ}$ C	50 $^{\circ}$ C
	Agitation time	1– 10 min	3 min
	Agitation speed	200 – 500 rpm	500 rpm
Reagent loading	Loading time	1– 10 min	3 min
Desorption	Time	1-15 min	10 min
	Temperature	150 – 250 $^{\circ}$ C	250 $^{\circ}$ C