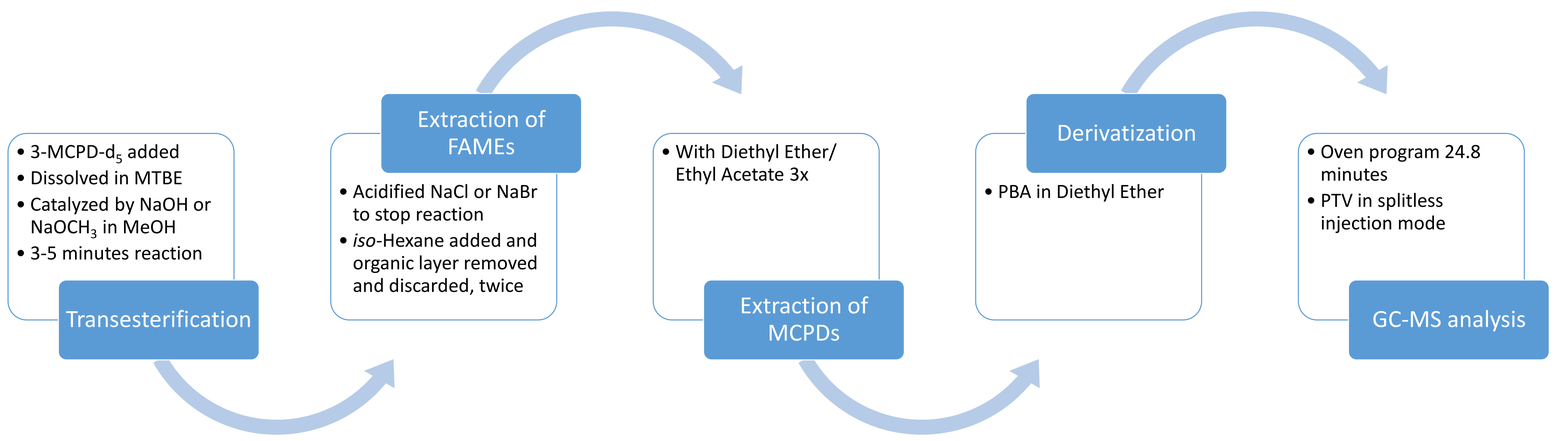
Optimizing GC-MS Analysis of 3-MCPD and Glycidyl Esters

Jana Rousova, Joe Konschnik, Hansjoerg Majer, Alexandria Pavkovich and Chris English
Restek Corporation, 110 Benner Circle; Bellefonte, PA, USA

Abstract

3-MCPD and glycidyl esters in edible oils are contaminants that are formed through refining processes. Several of these substances have been classified as possible human carcinogens. Methods, which are similar to one another, have been developed by ISO, AOCS, and DGF for analyzing these contaminants. While these methods cover extraction and derivatization techniques in detail, very little attention is paid to the GC-MS methods. With emerging automated systems, it is important to simplify and speed up the instrument method by optimizing the parameters, to include evaluating split injection.

Sample Preparation (according to AOCS Cd 13c-29)

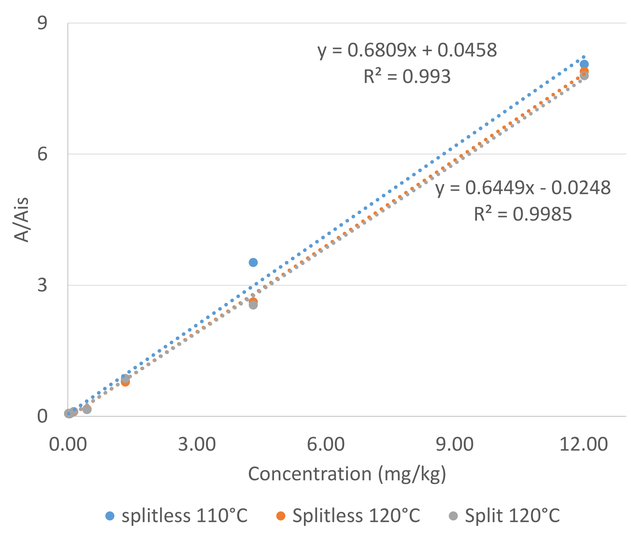


Optimization of GC-MS method

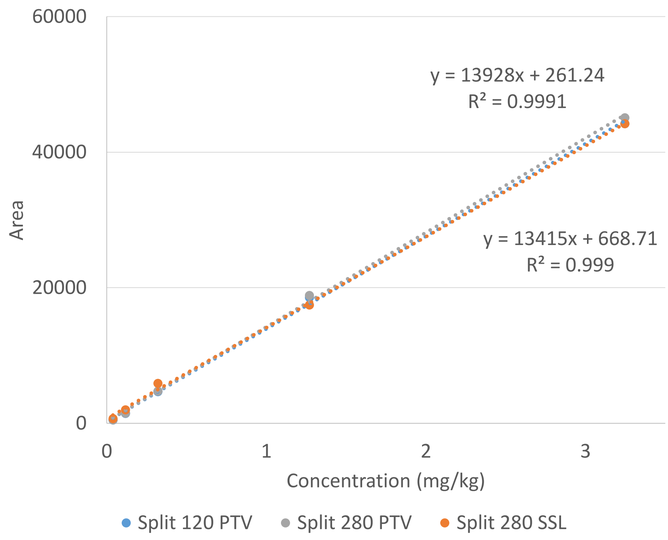
Initial temp. (°C)					
Splitless	RT1 (min)	RT2 (min)	Width1	Width2	Resolution
95	8.03	8.07	0.030	0.035	0.762
100	7.62	7.66	0.022	0.034	0.864
105	7.22	7.26	0.023	0.021	1.126
110	6.82	6.86	0.023	0.022	1.075
115	6.42	6.46	0.025	0.025	0.944
120	6.04	6.07	0.027	0.027	0.830
Split					
95	8.03	8.07	0.020	0.028	1.033
100	7.62	7.66	0.020	0.019	1.241
105	7.22	7.26	0.021	0.019	1.209
110	6.82	6.86	0.019	0.019	1.273
115	6.43	6.47	0.019	0.019	1.242
120	6.04	6.0	0.019	0.018	1.244

Optimization of GC-MS method – Evaluation of both split and splitless methods

Comparison of calibration curves for both split and splitless injections



Comparison of calibration curves for split injection at different temperatures/inlets

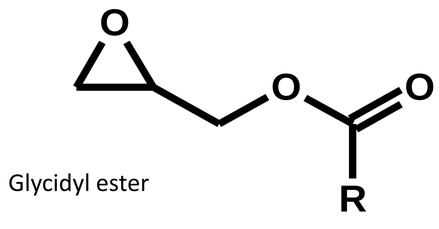


ProEZGC Model on Rxi-17Sil MS 30x0.25x0.25

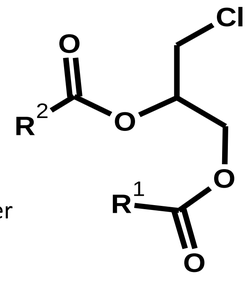
Pro *EZGC*® Chromatogram Modeler

Pro EZGC is a free GC modeler that allows for fast and simple optimization our analysis
Compounds currently present in the system:

- 3-MCPD and 3-MCPD-d5 derivatized with PBA
- 2-MCPD and 2-MCPD-d5 derivatized with PBA
- Glycidyl and glycidyl-d5 as 3-MBPD and 3-MBPD-d5 (resp.) derivatized with PBA
- Phenyl boronic acid (PBA)



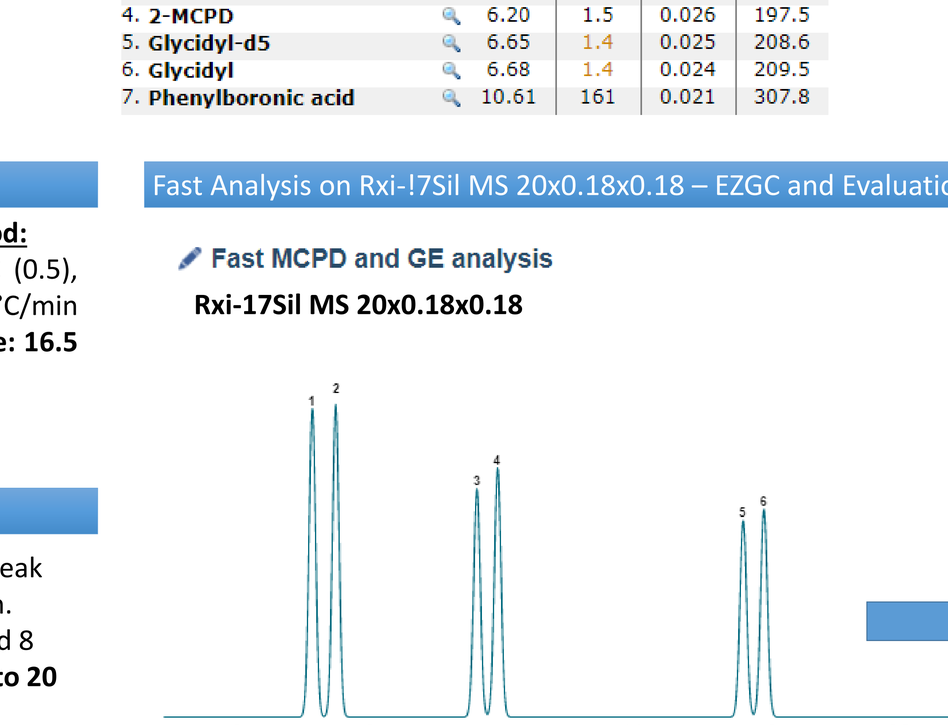
Glycidyl ester



3-MCPD ester

MCPD and GE analysis

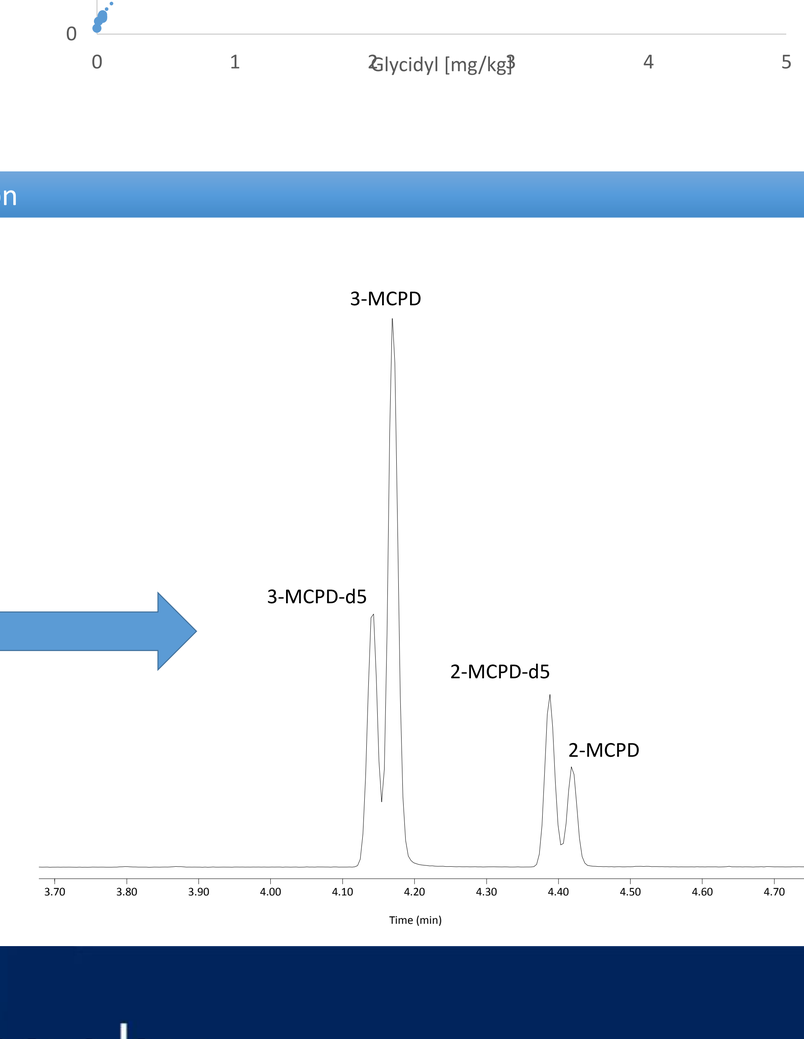
Rxi-17Sil MS 30mx0.25x0.25



Column: **Rxi®-17Sil MS**, 30.00 m, 0.25 mm ID, 0.25 µm (cat.# 14123)
Carrier Gas: Helium, Constant Flow @ 1.40 mL/min
Average Velocity: 44.27 cm/sec
Outlet Pressure (abs): 0.00 psi (Vacuum)
Oven Temp: 120 °C (hold 0.5 min) to 180 °C @ 12 °C/min to 330 °C @ 25 °C/min

Peaks	t_R (min)	R_S	Peak Width (min)	T_{peak} (°C)
1. 3-MCPD-d5	5.83	1.7	0.028	188.3
2. 3-MCPD	5.88	1.7	0.027	189.5
3. 2-MCPD-d5	6.16	1.5	0.026	196.5
4. 2-MCPD	6.20	1.5	0.026	197.5
5. Glycidyl-d5	6.65	1.4	0.025	208.6
6. Glycidyl	6.68	1.4	0.024	209.5
7. Phenylboronic acid	10.61	161	0.021	307.8

Evaluation on GC-MS/MS



Changing the GC-MS Method

Original method:
Temp program: 85°C (0.5), 6°C/min to 150°C, 12°C/min to 180°C, 25°C/min to 280°C (7); **total time: 24.8 min**
Splitless time 0.5-1 min

New, optimized method:
Temp program: 120°C (0.5), 12°C/min to 180°C, 25°C/min to 330°C (5); **total time: 16.5 min**
Split 10:1

Fast Analysis on Rxi-!7Sil MS 20x0.18x0.18 – EZGC and Evaluation

Fast MCPD and GE analysis

Rxi-17Sil MS 20x0.18x0.18

Column: **Rxi®-17Sil MS**, 20.00 m, 0.18 mm ID, 0.18 µm (cat.# 14102)
Carrier Gas: Helium, Constant Flow @ 0.81 mL/min
Average Velocity: 41.15 cm/sec
Outlet Pressure (abs): 0.00 psi (Vacuum)
Oven Temp: 120 °C (hold 0.5 min) to 200 °C @ 18.5 °C/min to 330 °C @ 35 °C/min

Conclusions

- An optimized GC-MS method led to improved peak shapes without detrimental effect on resolution. Manually optimized temperature program saved 8 minutes per analysis. **EZGC model can save up to 20 minutes.**
- Switching to split injection had no negative effect on limits of detection.
- Using regular split/splitless injector had no effect on the performance. However, using guard column is recommended.