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

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Abstract

3-MCPD and glycidyl esters in edible oils are contaminants that are formed through refining processes and 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 the method 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 method by optimizing the parameters, to include switching to split injection.

Changes to the AOCS CD 13c-29 Method

Several adjustments to the method were made to speed up the analysis. The original method is set up to focus the solvent (*iso*-octane), however, the analytes elute in second half of the run, making the initial low temperature and slow first ramp unnecessary. The second adjustment was to switch from splitless to split injection. Because considerable amount of derivatization agent will make it onto the column, regardless of PTV initial temperature, using split injection can improve the lifetime of column and other accessories. The last adjustment was to use regular split/splitless injector instead of PTV. Results of in-house testing showed improved peak shapes and no negative effects on the limit of detection.

Changing the Extraction Solvent

Initial solvent: ***iso*-hexane** replacement solvent: **heptane**

	iso-Hexane	Heptane	Combined
Recovery	99%	101%	103%
RSD	3%	1%	2%
	iC6 and C7	iC6 and comb.	C7 and comb.
t-test	0.13	0.08	0.35

Changing the GC-MS Method

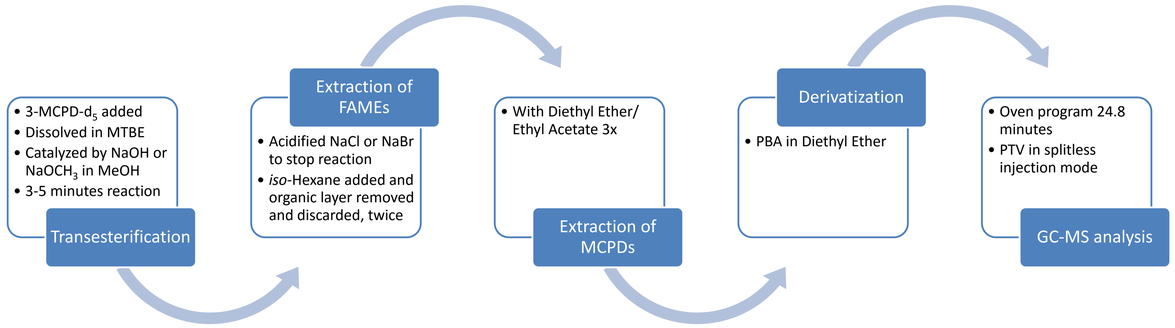
Original method:
Temp program: 85°C (0.5), 6°C/min to 150°C, 12°C/min to 180°C, 25°C/min to 280°C (7); **total time: 24.8 min**
Splitless time 0.5-1 min

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

Conclusions

- **No statistical difference between using *iso*-hexane and heptane.**
- **Optimized GC-MS method led to improvement of peak shapes without detrimental effect on resolution. Improved temperature program saves 8 minutes per analysis.**
- **Switching to split injection had no negative effect on limits of detection. In order to improve the limits, GC-MS/MS needs to be employed.**
- **Using regular split/splitless injector had no effect on the performance.**

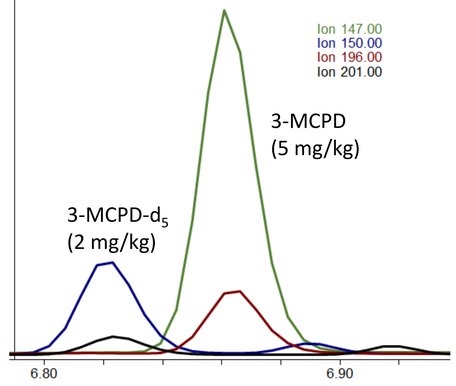
Sample Preparation (according to AOCS Cd 13c-29)



Optimization of GC-MS method – Initial temperature

Splitless					
Initial temp. (°C)	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

Splitless injection at 110 °C



Samples

- Soybean oil
- Extra Virgin Olive Oil (EVOO)
- Regular Olive Oil
- Walnut oil
- Grapeseed Oil

- Spiked Extra Virgin Olive Oil

Initial Oil Testing

Unaltered samples

	Assay A	Assay B	A-B
Soybean	0.55	0.41	0.13
EVOO	0.00	0.00	0.00
Olive oil	2.95	2.17	0.78
Walnut oil	2.8	0.22	2.58
Grapeseed oil	0.91	0.45	0.45

Spiked samples (5 mg/kg 3-MCPD and glycidyl)

	Assay A	Assay B	A-B	3-MCPD spike
Soybean	12.44	5.63	5.21	5.18
EVOO	13.06	5.05	4.88	5.16
Olive oil	16.06	7.39	5.22	5.03
Walnut oil	14.49	5.51	5.09	5.33
Grapeseed oil	13.07	5.61	4.76	5.26

Assay A – Glycidyl ester gets converted primarily to 3-MCPD and it as analyzed together with 3-MCPD already present
Assay B – Only 3-MCPD gets analyzed

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