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Determination of Fatty Acid Esters of 2- and 3-Monochloro-1,2-propanediol (MCPD) and Glycidol in Edible Oil Using GC/Triple Quadrupole MS

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Introduction

Esterified and free forms of 2-MCPD, 3-MCPD and glycidol (Figure 1) are heat-induced contaminants found in various types of processed food.[1] Following ingestion, esterified forms of these compounds are metabolised to the respective free forms which have been associated with a range of toxicities such as carcinogenicity and nephrotoxicity.

Various studies have investigated the levels of these contaminants in oils/fats from different sources and mitigation strategies are currently under development. Well-validated analytical methods are critical for these studies and currently, the American Oil Chemists' Society (AOCS) has adopted three methods for the analysis of these contaminants in edible oils and fats using gas chromatography-mass spectrometry.[2]

However, to support future studies where higher sensitivity and selectivity are necessary, analytical solutions based on triple-quadrupole mass spectrometer will be required. In the present study, a novel gas chromatography-triple quadrupole mass spectrometry (GC/TQMS) method was developed and validated for the simultaneous analysis of 2-MCPD, 3-MCPD and glycidyl fatty acid esters in edible oil. Subsequently, this method was applied for the quantitation of these contaminants in commercial edible oil samples.

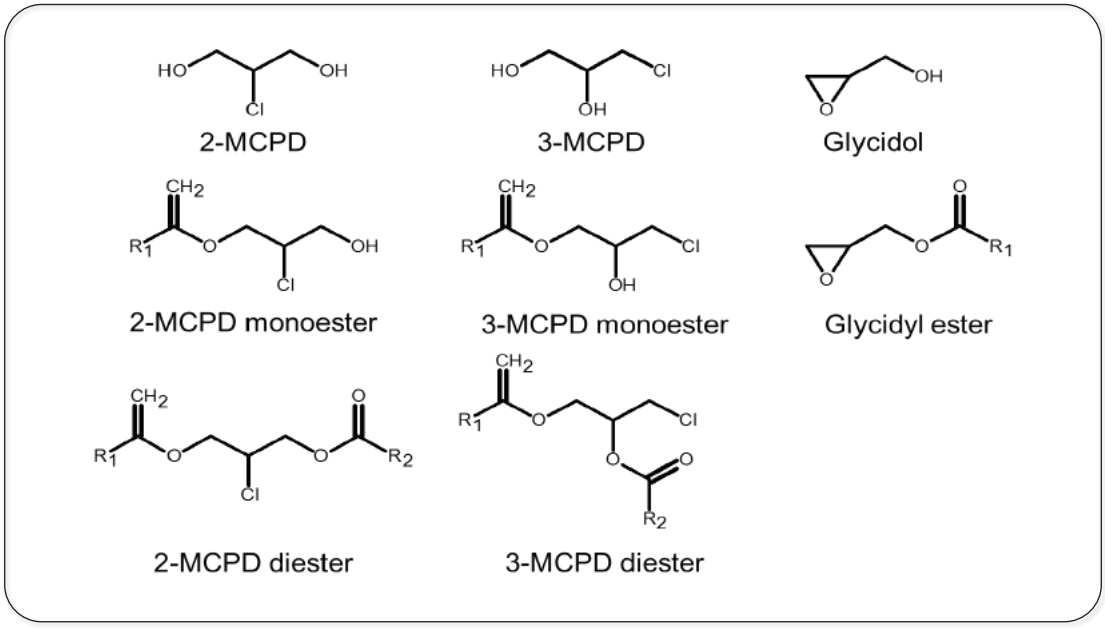

Figure 1. Structures of free and bound forms of 2-MCPD, 3-MCPD and glycidol.

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Methods and Materials

Fatty acid esters of 2-MCPD, 3-MCPD and glycidol in oil were extracted and derivatised using phenylboronic acid according to the validated AOCS Official Method Cd 29a-13.[2] The analyte standards used were 1,3-dipalmitoyl-2-chloropropanediol (PP-2-MCPD), 1,2-dipalmitoyl-3-chloropropanediol (PP-3-MCPD) and glycidyl palmitate (GlyP) (Toronto Research Chemical, Ontario, Canada).
The internal standards were 1,2-dipalmitoyl-3-chloropropanediol-d5 (PP-2-MCPD-d5) (Santa Cruz Biotechnology, and glycidyl palmitate-d5 (GlyP-d5) (Toronto Research Chemical, Ontario, Canada).

Cold-pressed extra virgin olive oil was used as blank matrix. For simplicity, the target analytes in this analysis are named as 2-MCPD, 3-MCPD and glycidol although the actual analytes are the derivatives.
The extracts were analysed on a GC/TQMS system (GCMS-TQ8040, Shimadzu Corporation, Japan). Separation was performed using a 30 m × 0.25 mm × 1.0 µm capillary column (SH-Rxi-1MS, Shimadzu Corporation, Japan). Detailed instrumental conditions are presented in Table 1 and MRM parameters for the different analytes are shown in Table 2.

Table 1. Instrumental conditions used for analysis

Parameter	Setting
GC conditions	
Injection mode/volume	: Splitless/0.5 µL
Injector temperature	: 250 °C
Flow control mode	: Pressure
Pressure	: 49.7 kPa
Oven temperature programme	: 80 °C (1 min) → 10 °C/min to 170 °C (5 min) → 3 °C/min to 200 °C → 15 °C/min to 300 °C → 300 °C (15 min)
MS conditions	
Interface temperature	: 300 °C
Ion source temperature	: 230 °C

Table 2. MRM parameters used in analysis

ISP	Start Time (min)	End Time (min)	Mode	Event Time (s)	Ch1 m/z	Ch1 CE	Ch2 m/z	Ch2 CE	Ch3 m/z	Ch3 CE	Ch4 m/z	Ch4 CE	Ch5 m/z	Ch5 CE
3-MCPD-d5	17.0	19.2	MRM	0.167	150.00>93.10	15	201.00>150.20	10	201.00>93.20	30	203.00>150.10	10	203.00>93.20	25
3-MCPD	17.0	19.2	MRM	0.133	147.00>91.10	15	196.05>91.20	25	147.00>65.10	25	198.10>147.20	15	-	-
2-MCPD	19.2	21.2	MRM	0.300	196.00>104.10	20	198.00>104.10	20	196.00>91.20	10	196.00>62.00	25	198.00>91.10	10
Glycidol-d5	21.2	23.0	MRM	0.167	150.00>93.10	15	245.00>150.10	10	247.00>150.10	10	245.00>93.10	25	247.00>93.10	25
Glycidol	21.2	23.0	MRM	0.133	242.00>147.10	10	240.00>147.10	15	240.00>91.20	30	242.00>91.10	25	-	-

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Results

MRM chromatograms of the analytes (using target MRM transitions) showed good peak shapes (Figure 2). The retention times of 3-MCPD-d5, 3-MCPD, 2-MCPD, glycidol-d5 and glycidol were approximately 18.4 min, 18.6 min, 19.6 min, 21.6 min and 21.7 min respectively.

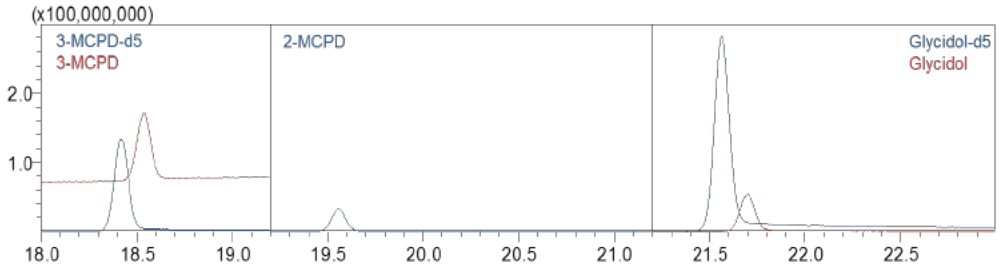

Figure 2. Representative MRM chromatogram where 3-MCPD-d5, 3-MCPD, 2-MCPD, glycidol-d5 and glycidol were eluted at 18.4 min, 18.6 min, 19.6 min, 21.6 min and 21.7 min, respectively.

Method validation was carried out to assess parameters such as sensitivity, accuracy, precision, linearity and repeatability using calibration standards or quality control (QC) sample. Subsequently, this method was applied for the quantitation of the different analytes in commercially available edible oil samples

Sensitivity

The sensitivity of the assay was examined by measuring the signal to noise (S/N) ratio of the analyte peaks. The was defined as S/N ratio of at least 5. The LOD (limit of detection) for this method was 0.003 µg of 2-MCPD and 3-MCPD and 0.006 µg of glycidol. The limit of quantitation (LOQ) was defined as S/N ratio of at least 10. The LOQ of this method was 0.01 µg of 2-MCPD and 3-MCPD and 0.024 µg of glycidol.

Linearity

Eight calibration standards ranging from 2-MCPD and 3-MCPD: 0.010 µg, glycidol: 0.024 µg to 2-MCPD and 3-MCPD: 0.930 µg, glycidol: 2.130 µg were used to construct the calibration curves. The calibration curves (Figure 3) for all analytes showed excellent linearity (R^2 > 0.998) (n = 6).

Repeatability

Excellent repeatability of the peak areas of consecutive injections were achieved for all analytes (< 3%) (n = 6).

Accuracy and Precision

QC samples at three concentrations (QC1, QC2 and QC3) were used to investigate the accuracy and precision of the method. High accuracy and precision were demonstrated for this method as the accuracy of the QC samples were all within 100 ± 7 % and the %RSD were all < 10% (n = 6).

Application of method for quantitation of analytes in commercially available edible oil samples

The validated method was applied for the quantitation of esters of 2-MCPD, 3-MCPD and glycidol in edible oil samples from different sources (Table 3, Figure 4). Generally, samples containing palm oil were found to contain the highest levels of the contaminants.

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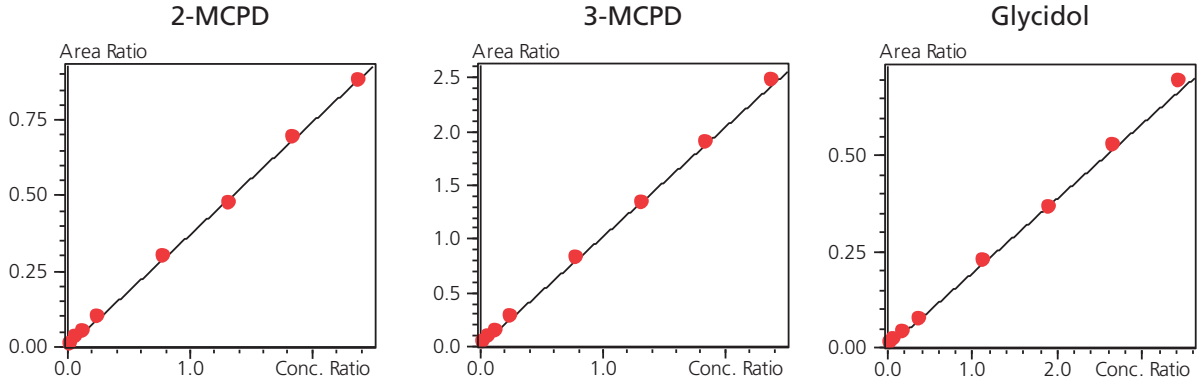

Figure 3. Calibration curves for the analytes 2-MCPD, 3-MCPD and glycidol where the x axis is the concentration ratio and y axis is the peak area ratio between analyte and IS peak areas.

Table 3. Concentration of contaminants in commercially available edible oil samples

Sample	Analyte Concentration (ppm) (n=3)		
	2-MCPD	3-MCPD	Glycidol
Kenaf seed oil	0.173 ± 0.007	0.354 ± 0.008	0.367 ± 0.003
Mustard oil	< LOQ	< LOQ	< LOQ
Olive oil	< LOQ	< LOQ	< LOQ
Palm oil A	2.820 ± 0.062	5.313 ± 0.032	8.813 ± 0.131
Palm oil B	0.653 ± 0.032	1.145 ± 0.023	5.891 ± 0.032
Peanut oil	0.491 ± 0.008	0.898 ± 0050	0.589 ± 0.016
Vegetable cooking oil*	1.346 ± 0.0182	2.804 ± 0.061	4.273 ± 0.046

*Vegetable cooking oil contains palm olein and soyabean oil

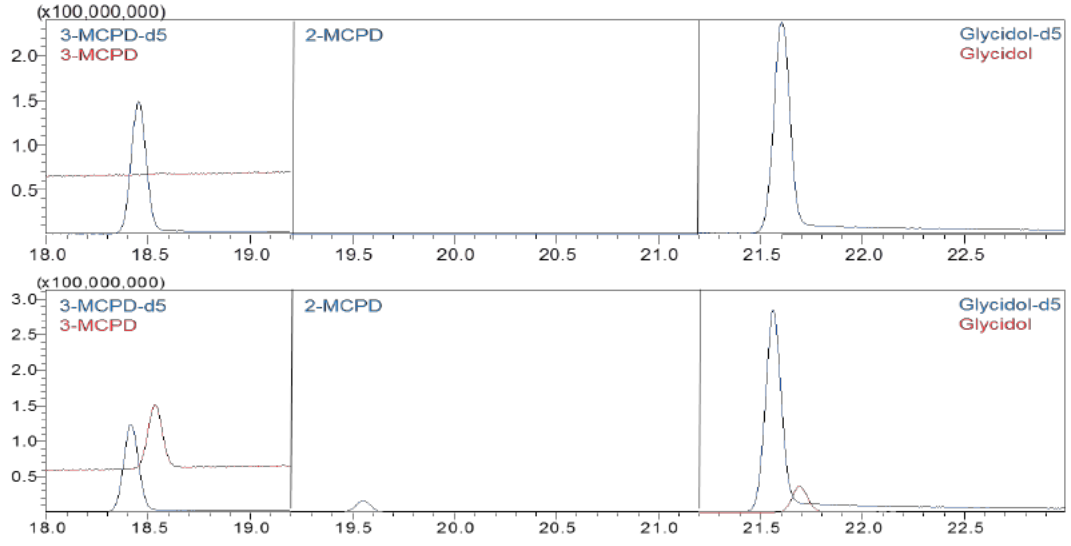

Figure 4. Representative MRM chromatograms of olive oil (top) and kenaf seed oil (bottom) shown below.

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Conclusions

In summary, a novel GC/TQMS method was developed and validated for the simultaneous analysis of 2- and 3-MCPD and glycidol fatty acid esters in edible oil. This method showed more than 3-fold improvement in sensitivity compared to the official method currently available and demonstrated excellent linearity, repeatability, accuracy and precision. Application of this method to the analyses of commercially available edible oil samples confirmed that samples containing palm oil show higher levels of contaminants.

References

[1] Federation for European Oil and Proteinmeal Industry. 2016. FEDIOL Q&A on 2- and 3-MCPD and Their Esters and Glycidyl Esters
[2] The American Oil Chemists' Society. 2013. 2- and 3-MCPD Fatty Acid Esters and Glycidol Fatty Acid Esters in Edible Oils and Fats by Acid Transesterification. AOCS Official Method Cd29a-13, Cd29b-13 and Cd29c-13

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