Forensic Chemistry: Differentiation of Olive Oil and Sunflower Oil by GCxGC-TOFMS and Determination of Fraudulent Material.

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Introduction

Genuine olive oil is prized in the food industry and its use has been associated with numerous health benefits. Among the most important of these are:

1. Extra virgin olive oil is high in polyphenols (a powerful antioxidant) and monounsaturated fat which contributes to lowering bad cholesterol.
2. Olive oil may be just as effective in the prevention of colon cancer as fresh fruits and vegetables.
3. Extra virgin olive oil may help to lower blood pressure.
4. Replacing other fats with olive oil may reduce the risk of Alzheimer's disease.
5. Olive oil promotes the secretion of bile and pancreatic hormones naturally and lowers the incidence of gallstones.

As such it commands higher prices than oils derived from other sources, and is regarded as an elite product. The opportunity then exists for unscrupulous merchants to label cheaper alternatives as genuine olive oil, and in this way to make much higher profits from these cheaper products. We have recently collaborated with the SAPS in the investigation of methods which can be used for the differentiation of olive oil from cheaper sunflower oil, and report here on the use of GCxGC-TOFMS in this application. Oil samples were provided by Superintendent W van Huyssteen, who also derivatised the oil samples to produce the fatty acid methyl esters (FAMEs) analysed in this study.

Samples

Six samples were investigated. One was a genuine sunflower oil which was pure and had been triply refined. Two were genuine olive oil samples, and the other three were suspect samples sold as olive oil, either as Extra Virgin or Virgin Cold Pressed. Methylation of the samples to produce FAMEs was conducted before analysis.

Analysis Conditions

GCxGC Parameters: Agilent 7890N

1st Dimension Column:	Rxi-5SilMS; 30 m x 0.25 mm x 0.25 µm
2nd Dimension Column:	Rtx-200; 2 m x 0.18 mm x 0.2 µm
Injector temperature:	250ºC
Inlet:	S/SL in the split (10:1) mode.

Primary Oven:	40ºC (2 min), to 160ºC at 30ºC/min, to 250ºC at 2ºC/min.
Secondary Oven:	50ºC (2 min), to 170ºC at 30ºC/min, to 260ºC at 2ºC/min.
Modulator offset:	30ºC
Modulation period:	5 sec.
Flow rate:	1 ml/min. Helium at constant flow.
Total run time:	51 min.

MS Parameters: Pegasus HT GC-TOFMS

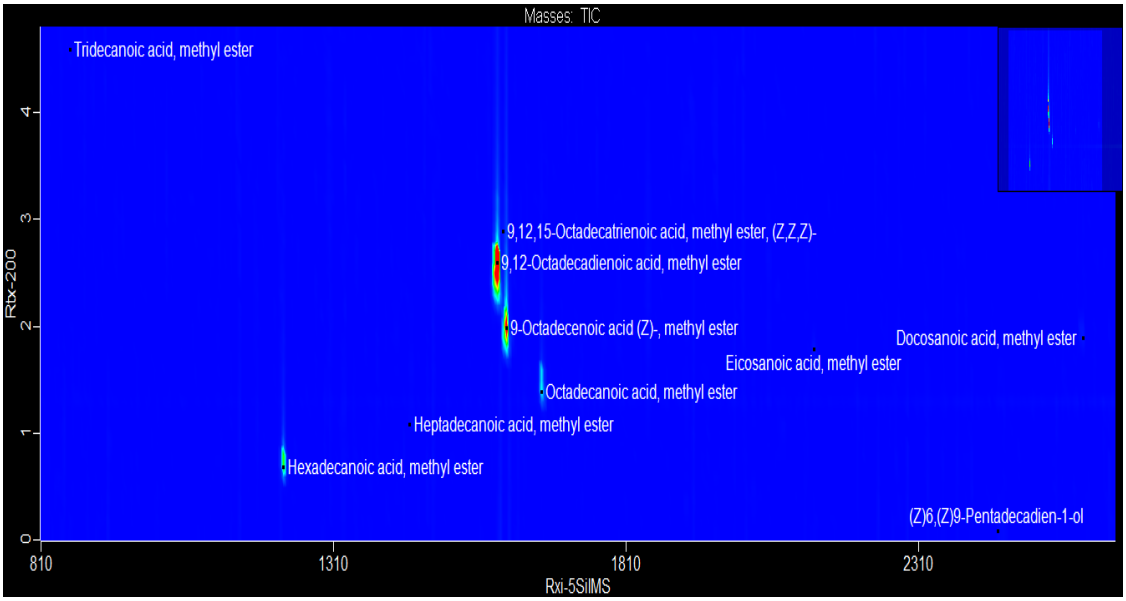
Mass range:	40 to 450 u.
Acquisition rate:	100 spectra / second
Ion source temperature:	240ºC
Transfer line temperature:	250ºC

Results and Discussion

Reference Samples

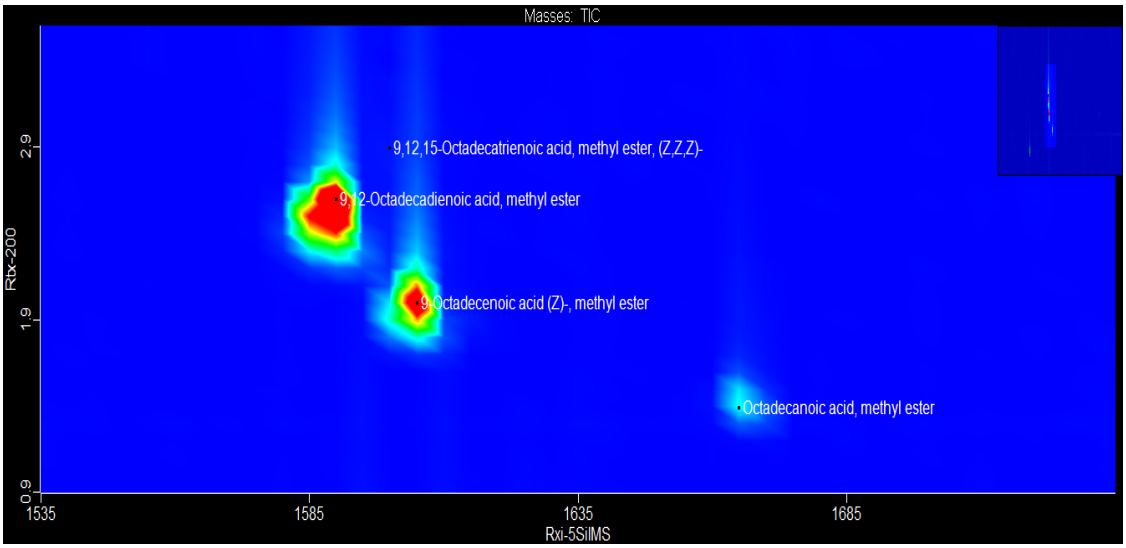
The six samples were analysed using the methods described above. A typical chromatogram is shown below for the sunflower oil reference sample (*Figure 1*).

Figure 1: Total ion chromatogram (TIC) of the sunflower oil reference sample.



The area in the chromatogram of interest in differentiating the different oils is that involving the different C_{18} fatty acids, and this area is shown below for the sunflower oil reference sample (*Figure 2*).

Figure 2: TIC of the C_{18} area of the sunflower oil reference sample.



In the sunflower oil sample the 9,12-Octadecadienoic acid methyl ester is the most abundant peak (43.55%) with the 9-Octadecenoic acid methyl ester accounting for only 24.41% of the components as is shown in Table 1.

Table 1: Partial peak table for the sunflower oil reference sample.

Peak #	Name	Similarity	1st Dimension Time (s)	2nd Dimension Time (s)	Quant Masses	Area %
4	9,12-Octadecadienoic acid, methyl ester	946	1590	2.6	67	43.57
5	9,12,15-Octadecatrienoic acid, methyl ester	833	1600	2.9	79	0.16
6	9-Octadecenoic acid, methyl ester	950	1605	2.0	55	24.42
7	Octadecanoic acid, methyl ester	929	1665	1.4	74	11.28

By comparison the olive oil reference samples (*Figures 3* and *4*) contain far more of the 9-Octadecenoic acid methyl ester relative to the 9,12-Octadecadienoic acid methyl ester, as is shown in the peak tables presented in *Tables 2* and *3*.

Figure 3: TIC of the C_{18} area of the olive oil reference sample 1.

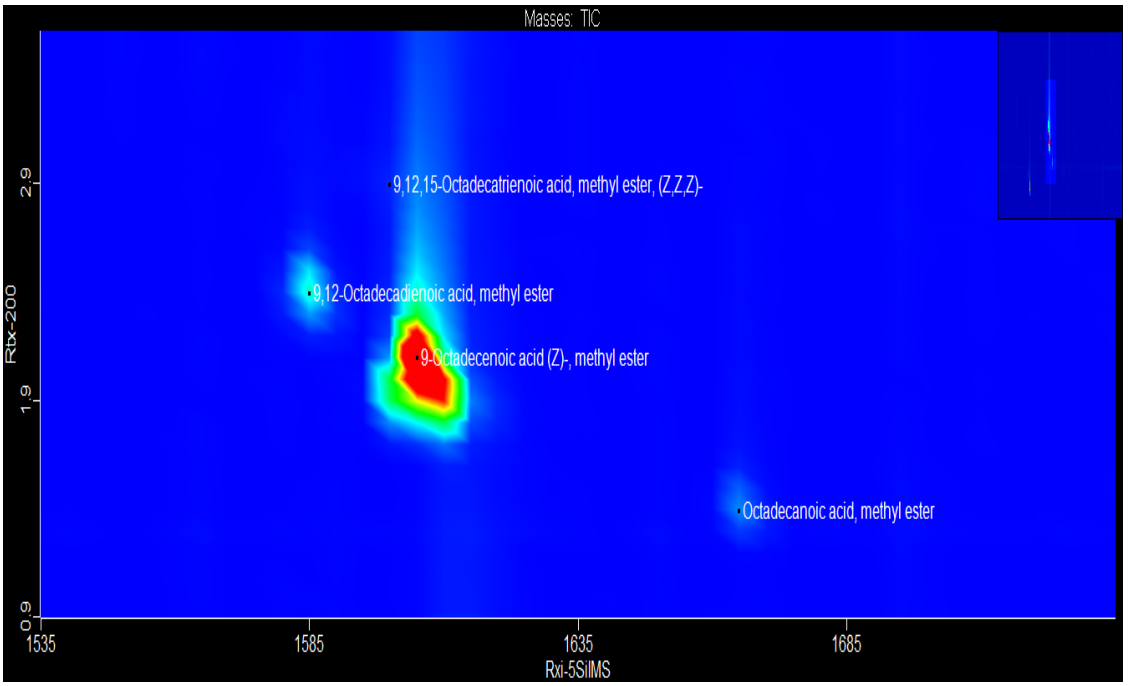


Figure 4: TIC of the C_{18} area of the olive oil reference sample 2.

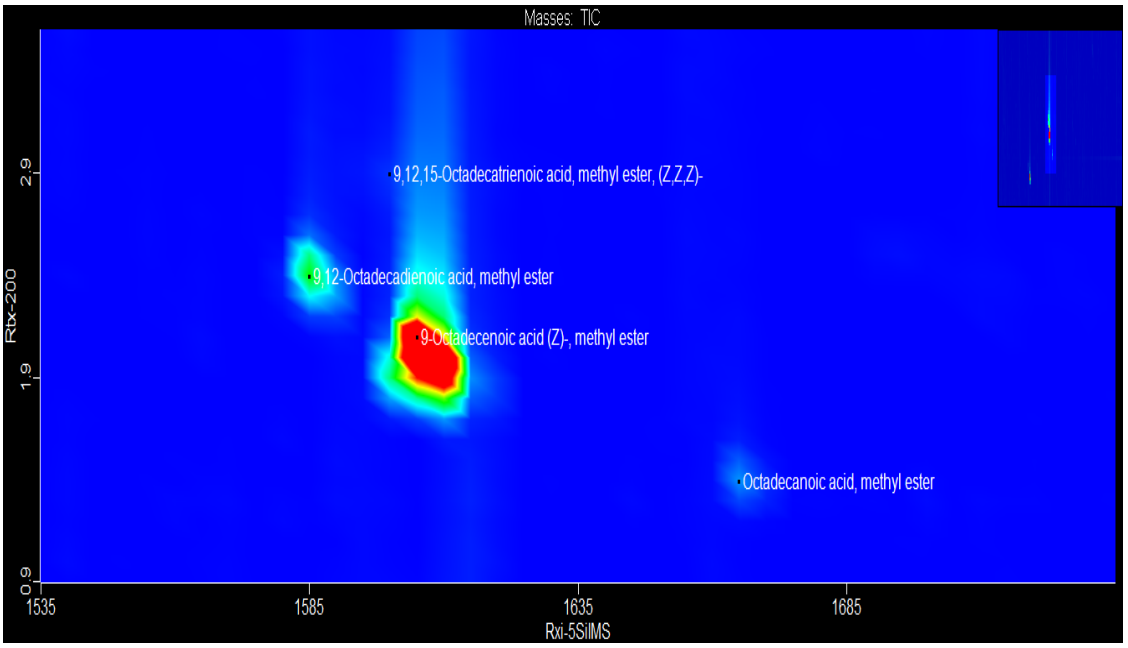


Table 2: Partial peak table for the olive oil reference sample 1.

Peak #	Name	Similarity	1st Dimension Time (s)	2nd Dimension Time (s)	Quant Masses	Area %
4	9,12-Octadecadienoic acid, methyl ester	950	1585	2.4	67	4.44
5	9,12,15-Octadecatrienoic acid, methyl ester	849	1600	2.9	79	0.40
6	9-Octadecenoic acid, methyl ester	949	1605	2.1	55	60.38
7	Octadecanoic acid, methyl ester	915	1665	1.4	74	4.83

Table 3: Partial peak table for the olive oil reference sample 2.

Peak #	Name	Similarity	1st Dimension Time (s)	2nd Dimension Time (s)	Quant Masses	Area %
5	9,12-Octadecadienoic acid, methyl ester	947	1585	2.4	67	6.22
6	9,12,15-Octadecatrienoic acid, methyl ester	908	1600	2.9	79	0.42
7	9-Octadecenoic acid, methyl ester	947	1605	2.1	55	56.74
8	Octadecanoic acid, methyl ester	924	1665	1.4	74	4.03

While there is a slight difference in the relative amounts of the components in the two olive oils the overall trend, relative to the sunflower oil, is quite apparent and this property can then be used to identify the oil present in the suspect samples.

Suspect Samples

The three suspect samples could then be analysed and the likelihood of them being olive oil based could be evaluated on the basis of the results obtained above, bearing in mind that for the olive oil samples we expect far more of the 9-Octadecenoic acid methyl ester relative to the 9,12-Octadecadienoic acid methyl ester.

The chromatograms for these three samples are shown in *Figures 5, 6* and *7*, and the partial peak tables for the three samples are shown in Tables *4, 5* and *6*.

Figure 5: TIC of the C_{18} area of the suspect oil sample 1.

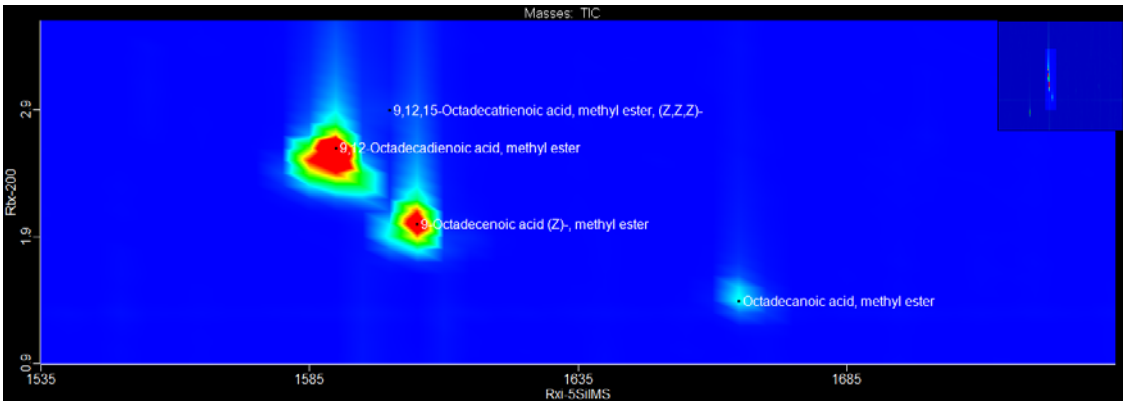


Figure 6: TIC of the C_{18} area of the suspect oil sample 2.

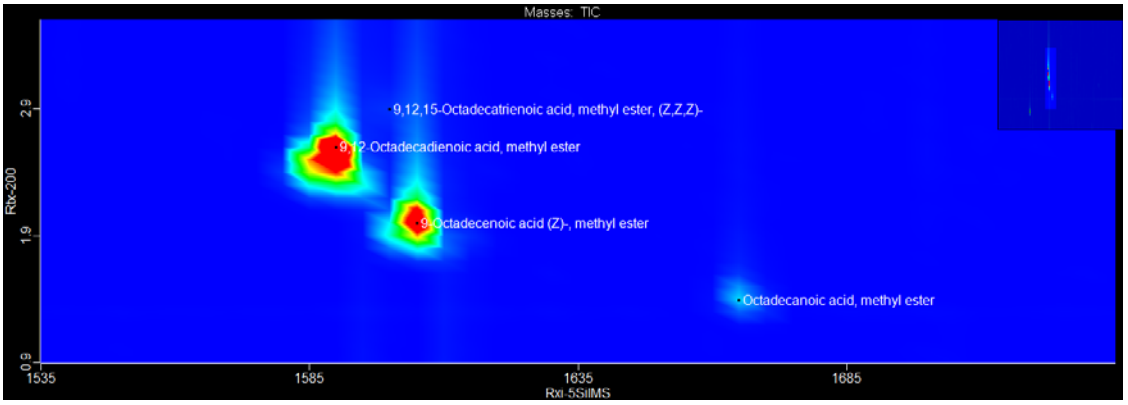


Figure 7: TIC of the C_{18} area of the suspect oil sample 3.

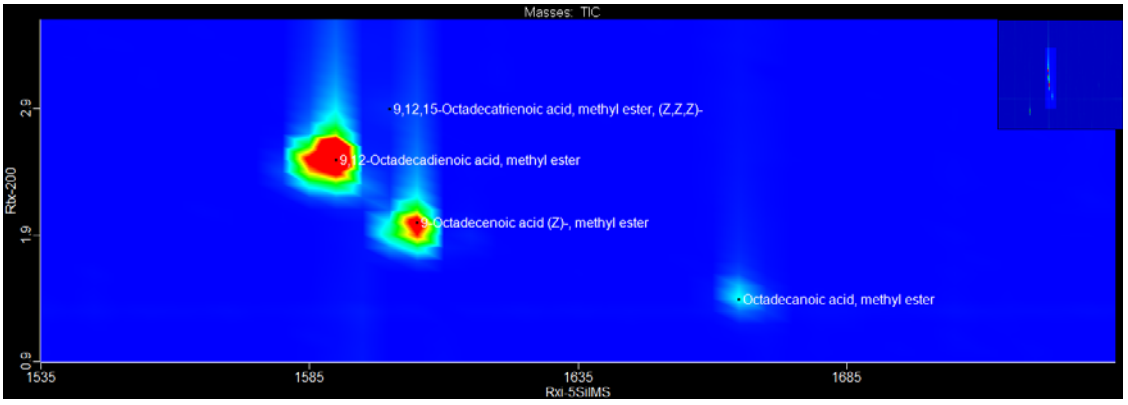


Table 4: Partial peak table for the suspect oil sample 1.

Peak #	Name	Similarity	1st Dimension Time (s)	2nd Dimension Time (s)	Quant Masses	Area %
4	9,12-Octadecadienoic acid, methyl ester	948	1590	2.6	67	46.13
5	9,12,15-Octadecatrienoic acid methyl ester	858	1600	2.9	79	0.30
6	9-Octadecenoic acid methyl ester	944	1605	2.0	55	25.20
7	Octadecanoic acid, methyl ester	928	1665	1.4	74	10.10

Table 5: Partial peak table for the suspect oil sample 2.

Peak #	Name	Similarity	1st Dimension Time (s)	2nd Dimension Time (s)	Quant Masses	Area %
4	9,12-Octadecadienoic acid, methyl ester	951	1590	2.6	67	43.49
5	9,12,15-Octadecatrienoic acid methyl ester	886	1600	2.9	79	0.37
6	9-Octadecenoic acid methyl ester	950	1605	2.0	55	28.82
7	Octadecanoic acid, methyl ester	924	1665	1.4	74	7.68

Table 6: Partial peak table for the suspect oil sample 3.

Peak #	Name	Similarity	1st Dimension Time (s)	2nd Dimension Time (s)	Quant Masses	Area %
3	9,12-Octadecadienoic acid, methyl ester	944	1590	2.5	67	46.80
4	9,12,15-Octadecatrienoic acid methyl ester	894	1600	2.9	79	0.30
5	9-Octadecenoic acid methyl ester	950	1605	2.0	55	24.27
6	Octadecanoic acid, methyl ester	917	1665	1.4	74	10.12

As can be seen from the partial Peak tables above the values for the compounds present in the three suspect samples are highly similar to those obtained for the sunflower oil reference sample, and are totally different for what would be expected if the samples did indeed consist of olive oil. It can then be safely concluded that the three suspect samples do not consist of olive oil, but instead are sunflower oil, fraudulently labelled to obtain greater profit.

Conclusion

GCxGC-TOFMS provides a quick and conclusive method for the differentiation of olive oil and sunflower oil. Major differences occur in the relative amounts of the C_{18} FAME components, and these differences provide an unambiguous means of differentiating between the two oils.

On the basis of this methodology it could be shown that three suspect samples were fraudulently labelled as olive oil, and that the major component in the samples was in fact sunflower oil.