DETERMINATION OF FAME IN GASOLINE

–A FUEL QUALITY ANALYSIS

BSc in Chemical Engineering
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Abstract

Gasoline is produced by distilling petroleum oil. This is done at a refinery, where a lot of other products are produced as well. With increasing interest in bio-fuels the fuel companies started to produce substances such as biodiesel as well as the petroleum-based fuels. These products are then transported to where they are going to be used or sold, there included both gasoline, which is a petroleum-based fuel, and biodiesel (FAME), which in Sweden is based on rapeseed oil. If the vessel for transporting gasoline, or pipeline/connections filling and emptying the tanks, has previously been used for biodiesel, there is a risk of contaminating the gasoline with biodiesel. This contamination can have a lot of different effects such as either clogging filters or injectors in both gasoline- and ethanol-based engines, or even change the properties and therefore quality of the fuel.

To ensure that the results from tests and research involving gasoline can be used and compared with each other, the quality of the fuel must have the same properties throughout all tests. This is controlled by taking samples on a regular basis and analyzing the quality and level of impurities in the fuel used in that specific test. Screening for FAME is therefore necessary which is where this thesis becomes relevant.

This thesis was carried out with the purpose to develop a new or verify an already developed method to quantify FAME in gasoline. To determine the FAME content, a standard gas chromatography method, IP 585, was used. It was changed to fit in this application, since it was originally made to determine FAME content in diesel, not gasoline.

It was concluded that it was possible to determine the FAME content in gasoline when IP 585 was used as is. There were some possible alternatives to IP 585 and they will be discussed in the literature study.

Sammanfattning

Bensin framställs genom destillation av råolja. Detta görs på ett raffinaderi där ett flertal andra produkter också utvinns. På senare tid har ögonen öppnats för "biobränslen", bland annat biodiesel. Det händer därför att detta också framställs på samma plats som bensinen. Dessa produkter säljs sedan och brukar fraktas i stora tankar till företagen som köpt dem. Ifall tankarna vid transport eller rören bränslet går igenom till tankarna först använts till biodiesel och sedan används till bensin finns det stor risk att en del biodiesel hamnar i bensinen. Detta kan leda till en rad olika problem. Ett exempel är att biodieseln kan sätta igen och förstöra injektorer i bensin- och etanolmotorer. Det kan även påverka testresultat i olika testriggar, vilket är ett av fallen på Volvo. Ifall bränslet inte bibehåller samma kvalitet för varje test det används i leder det till svårigheter vid jämförelser och resultatens riktighet. Det blir därför nödvändigt att kontrollera bensinens innehåll, där inräknat screening av FAME.

Detta arbete utfördes med syftet att utveckla en ny eller verifiera en redan beprövad metod för att bestämma koncentrationen FAME i bensin. För att mäta koncentrationen FAME användes en standardmetod till GC-MS, IP 585. Den modifierades något för att passa in i denna applikation då den från början var gjord för kvantifiering i diesel och inte bensin.

Slutsatsen drogs att det är möjligt att mäta koncentrationen FAME i bensin med IP 585 använd som den är. Det fanns möjliga alternativ till metoden, dessa bemöts i litteraturstudien.

Abbreviations:

GC-MS	Gas Chromatography Mass Spectrometry
FAME	Fatty Acid Methyl Esters
FAEE	Fatty Acid Ethyl Esters
RME	Rapeseed Methyl Ester
TIC	Total Ion Current
MSD	Mass Selective Detector (Quadrupole mass spectrometer)
SIM	Selected Ion Monitoring

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1 INTRODUCTION

This thesis was carried out with the purpose to develop a new or apply an already existing method to quantify FAME in gasoline at Volvo Cars Torslanda. Three main questions were considered in the making of this thesis.

- Is it possible to use a GC-MS to accurately determine the concentration of different FAME in gasoline?
- Are there any alternative methods to the one the external lab uses?
- Is the standard method IP 585 adjustable to a non-polar column?

Volvo Cars is a global company which specializes in building cars. One part of Volvo is situated in Torslanda, Göteborg. Apart from building and designing cars here, a lot of tests are held here to ensure the quality of the cars. The different tests range from fuel quality to corrosion and emission tests.

Prior to this thesis Volvo was buying this kind of sample testing from an external lab where they used IP 585 standard method for determination of FAME. This method was therefore considered as functional, other methods were still evaluated in the literature study for comparison and the possibility of finding an even better method.

Since the lab at Volvo mostly uses GC-MS with non-polar columns it would be more efficient if IP 585 could be applied when using a non-polar column as well.

The thesis will only include testing of one method at a well-defined detection range, 4.5 to 150 mg/kg (ppm). Samples with higher concentrations than specified in the standard will be diluted until they are within the interval.

Only FAME from methyl hexadecanoate (C16:0) to methyl octadecatrienoate (C18:3) will be analysed as stated in IP 585.

1.1 Background

Gasoline is used internally at Volvo in a variety of testing rigs. Gasoline is purchased and delivered from external suppliers. To ensure the fuel quality, sample tests are carried out on a regular basis. This includes screening for FAME.

If FAME contaminated gasoline is used at a testing rig or out on the field, it can lead to a lot of different problems. First and foremost, if the quality/properties of the gasoline used differ from test to test, it would be difficult to compare results. Second, since FAME might clog filters and fuel injectors on gasoline and ethanol engines it can lead to engine failure and expensive repair costs for the customer. Third, FAME might dilute engine oil if it gets past the pistons down into the oil thus "aging" it.

One of the reasons FAME can end up in gasoline to begin with is if the vessel for transporting gasoline previously has been used for biodiesel and was not thoroughly cleaned between uses. It can also contaminate gasoline if the connections and tubes used to fill and empty the tanks have been used for diesel or biodiesel. If FAME is detected, the sample is sent to an external lab for measuring the concentration. To send these tests is expensive and it takes a couple of days to get a response, therefore to find or develop a method for determining FAME that can be used internally would save a lot of time and money.

Initially a literature study was carried out where reports using the same kind of analysis were evaluated. In table 1 below, the aim, instrument used, accuracy and conclusion are presented. The columns with comments and reliability are conclusions made by the writer of this thesis.

Search engines used:

Primo – University of Borås' own search engine

https://hb-se-primo.hosted.exlibrisgroup.com/primo-explore/search?vid=46BORAS_V10

Google Scholar – Google's search engine specifically made for scientific articles

http://Scholar.google.se

Google Search – Google's multi-purpose search engine.

http://www.google.se

Table 1: All studies gathered and relevant data summarized.

Study/ Literature	Purpose/Aim	Method	Range	Conclusion	Comment	Reliability
Mayo, C.M. et al. (2015)	To develop a simple, quick and green method for determination of FAMEs in biodiesel made from waste frying oil.	GC-FID	µg/L	The method works on biodiesel made from waste frying oil.	Not relevant, FAME is not measured in diesel or gasoline	Peer-reviewed and published in a well-known journal. Should be reliable.
Sitko et al. (2011)	To develop a new method for measuring FAME in biodiesel using EDXRF.	EDXRF	>~0,7 vol%	The method is considered to have potential regarding analysis of diesel.	Is probably too difficult to be used in this application	-"-
Swedish Standards Institute (SIS) (2014)	A standard method to determine the FAME concentration in diesel or lamp oil using FT-IR.	FT-IR	>0,05 vol%	The method as such works	Not sensitive enough.	A standard which SIS distributes. Should be trustworthy.
Energy Institute (EI) (2010)	A standard to determine FAME, derived from bio-diesel fuel, in aviation turbine fuel using GC-MS with SIM/Scan detection method.	GC-MS	4,5–150 mg/kg	The method as such works.	A possible option	A well-used standard. Should be very reliable.
Borges et al. (2011)	To find a connection to determine FAME concentrations in diesel using its viscosity correlation.	Rotation viscometer	--	--	Probably difficult to apply since different gasolines is analysed.	Peer-reviewed and published in a well-known journal. Should be reliable.
Chuck et al. (2010)	A study which purpose is to evaluate the possibilities of today to measure the quality of biodiesel.	Multiple	--	--	Not relevant in this application.	-"-

In the report written by Mayo et al., the results are not critically discussed, and it seems as the researchers are fully relying on the method throughout the whole discussion. There is no discussion regarding the method's potential weaknesses either, but the focus lies in highlighting all the benefits instead. However, the result is compared with other reports where other methods were used. The conclusions agree with the result.

Sitko et al. openly discuss their results from a critical point of view, bring up problems and try to mention results and conclusions that can be helpful to similar projects. They also discuss weaknesses and strengths in the report such as increasing standard deviation in lower concentrations.

The report from EI is a standard method. It does not contain any discussion or results. The procedure is easy to follow.

Regarding the report measuring concentration using a viscometer, Borges et al. (2011), it was realised after reading the report that it will not be applicable in this application. Another comment regarding this report is that the discussion and result part is very short and does not offer the reader to thoroughly get familiar with the project.

After a discussion with the supervisors the decision was made that the same method used in the external lab was going to be used: **IP 585**.

1.2 Theory

1.2.1 GC-MS

GC-MS is short for Gas Chromatography – Mass Spectrometry and consist of two different analytical methods. The methods are executed by a gas chromatograph and a mass spectrometer.

Gas chromatography can be summarised as an analysis where a sample is injected with a syringe into an injector which leads the sample into a tube, *a column*, where the different components of the sample are separated (V.G. Berezkin & V.R. Alishoyev & I.B. Nemirovskaya 1977). The column is set inside an oven that can both keep a certain temperature and change it over time. This serves two purposes: to keep the sample from condensing inside the column and to affect the traveling speed. At the end of the column a detector analyses the components as they pass. Two major components of interest, which have the greatest impact on sample separation and detection, are the column and detector.

As the sample enters the injector it is vaporised and in some cases part of the injection is vented with a split injector. Since just a part of the sample injected reaches the column it reduces the risk of overloading the column (H.M. McNair & J.M. Miller 2009 pp. 20-21; V.G. Berezkin & V.R. Alishoyev & I.B. Nemirovskaya 1977). A carrier gas then leads the sample through the column.

The most common type of columns used is capillary columns, also referred to as open tube columns. A capillary column is basically a very thin tube which's inside surface is coated with a material with defined chemical properties; this is referred to as the stationary phase (H.M. McNair & J.M. Miller 2009 pp. 84). To transport the sample through the column a carrier gas is used, also referred to as the mobile phase. The carrier gas used in this application is helium, but both hydrogen and nitrogen can be used as carrier gas (H.M. McNair & J.M. Miller 2009 pp. 15). As mentioned above the sample travels through the column and the different

components get separated. This is because different substances react differently to temperature and have different affinity to the solid phase, thus traveling at different speeds through the column and therefore leaving the column at different times even though they are injected at the same time. Imagine two substances that react to the column in the same way, but they have different boiling points, an increase in temperature will then affect the elution making the substance with a lower boiling point elute faster. This works the other way around as well, such as two substances having very similar boiling points but different affinity to the column. The temperature can be controlled and adjusted depending on the substances analysed or method used. The time between a component enters and leaves the column is called *retention time*. This is the basic principle of chromatography (H.M. McNair & J.M. Miller 2009 pp. 5).

When the component leaves the column, it enters a mass spectrometer. It acts as the detector in this application. It has some parameters that can be changed. One of these parameters is when the MSD should start analysing the sample leaving the column, this is regulated by a so called solvent delay. Other parameters such as SIM and scan are explained further down.

A mass spectrometer is an instrument that analyses mass on the different types of molecules in a sample. When a sample enters the instrument, it is first bombarded with electrons which have the purpose of ionizing the molecules of the sample. The molecules are then sent through an electromagnetic field that is changing depending on the desired molecule weight to be analysed at the detector at the end of the field. The molecules are affected differently depending on their mass to charge ratio which makes their trajectories differ and thus allowing the detector to tell them apart. The signal amplitude increases with substance concentration making quantifying possible (J. H. Gross 2013 pp. 3).

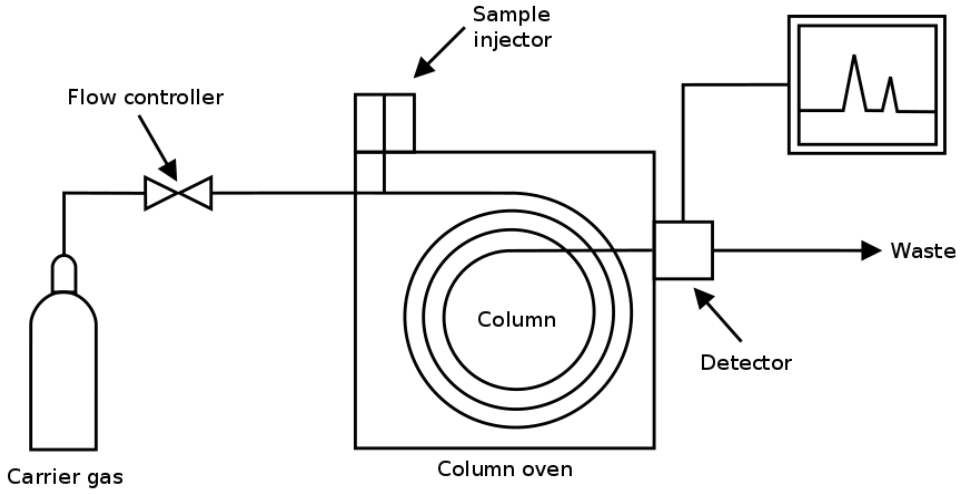

Figure 1: By Offnfopt - created using File:Gas chromatograph.png as a reference, Public Domain, https://commons.wikimedia.org/w/index.php?curid=39498676

Figure 1 shows a rough image of the different components in a GC. The detector in this case would be an MSD.

There are two main method of analysis in an MSD, scan and SIM (Selective Ion Monitoring). When using a scan method, the MSD continuously alternates the radio frequency to "always" scan for all possible ions within the spectrum range of the detector. This leads to a decrease in accuracy since some of the ions entering the detector, while the radio frequency is adjusted to another ion, will not pass through the quadrupole at that given time. SIM on the other hand

only scans for ions specified by the user or method used and thus making the instrument a lot more sensitive and accurate since the relative time the machine spends searching for the desired ions is longer. If the MSD is set to look for only one single ion, it will detect close to 100% of the ions entering the MSD. The results of a scan are then presented in a so-called TIC, Total Ion Current which basically is amplitude of detected ions plotted over time (Agilent Technologies 2013).

1.2.2 Gasoline

Gasoline mostly consists of saturated hydrocarbons and is derived from petroleum oil (Britannia Academic 2018). It should be noted that the petrol ether partition of gasoline does not consist of esters, only non-polar hydrocarbons with size ranges from 4 to 12 carbon atoms, generally shorter than FAME (Nationalencyklopedin 2018). Gasoline can contain by products such as benzene, toluene and other aromatic hydrocarbons.

When used as vehicle fuel, additives such as anti-oxidants are commonly used to improve the quality of the fuel. The composition might also be different depending on climate since gasoline requirements are depending on the temperature where it is sold (Swedish Standards Institute (SIS) 2012). For example, vapor pressure of gasoline in cold climate such as during winter or in otherwise colder countries is often higher than that of the summer. Higher vapour pressure means that the petrol ether partition will consist of shorter carbon chains than gasoline with lower vapour pressure.

1.2.3 Fatty Acid Methyl Ester

FAME is an abbreviation for fatty acid methyl esters; the ME-part is derived from the fact that Methyl Esters are produced. This is through a transesterification where an alcohol and fatty acids can react in presence of a catalyst. The reaction yields esters and glycerol. In this case methanol is used to produce methyl esters, if ethanol were to be used; ethyl esters (FAEE) would be produced instead. RME is an example of a fatty acid methyl ester. (Hoekman et al. 2011)

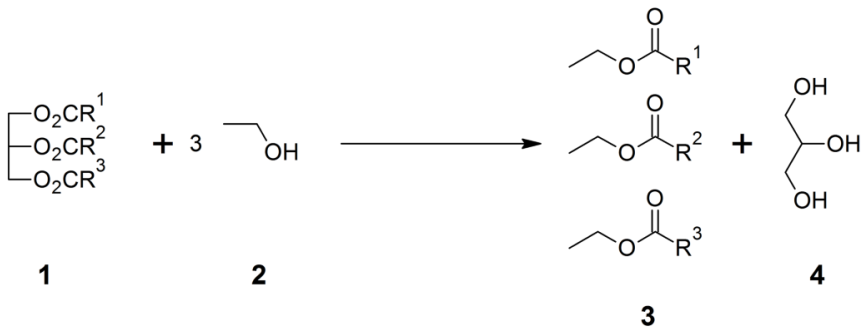

Figure 2: By "Self" - Public Domain, https://commons.wikimedia.org/w/index.php?curid=11705929

Figure 2 illustrates the reaction in a transesterification process. A triglyceride (1) reacts with an alcohol, in this case ethanol (2) in the presence of a catalyst where fatty acid ethyl esters (3) and glycerol (4) are produced.

Since there are a lot of different fatty acids and alcohols, there are a lot of different fatty acid esters. The differences between different FAME-based bio fuels can be explained with their fatty acid –profiles, i.e. which fatty acids the FAME in the solution consist of. The oil used is not necessarily monodisperse and so the FAME made from it will not be either. Two main factors changing the properties of a FAME are what molecule sizes are present within the fuel

and their degree of saturation. Generally, lower saturated FAME are less resistant to oxidation. (Hoekman et al. 2011)

Depending on what source of fatty acids used in production the fatty acid size partitions vary. The most common sizes are in the range of 12-22 carbon atoms. It should also be mentioned that the properties of FAME can be different, even when derived from the same source, depending on the production method, how long it has been stored and under what conditions. Handling and storing greatly affects quality and durability of FAME. (Hoekman et al. 2011)

1.2.4 Standard IP 585

This method was, as mentioned before, created for determination of FAME in aviation turbine fuel. Thus a few changes had to be made for it to be applicable in this scenario. The first difference was that the samples were based on gasoline and not white spirit in this application, also heptane was used as syringe cleaner and solvent instead of cyclohexane. Chloroform and cyclohexane was used for column cleaning between samples. Moreover, the external standards were initially made with gasoline and not dodecane to have as many similarities as possible between the samples and other solutions. This was later changed back to the original dodecane as solvent.

Table 2: The different FAME analyzed in the method and abbreviations used when referring to them.

Fatty Acid Methyl Ester	Molecular Formula	Symbol Used
Methyl hexadecanoate (methyl palmitate)	$C_{17}H_{34}O_2$	C16:0
Methyl heptadecanoate (methyl margarate)	$C_{18}H_{36}O_2$	C17:0
Methyl octadecanoate (methyl stearate)	$C_{19}H_{38}O_2$	C18:0
Methyl octadec*en*oate (methyl oleate)	$C_{19}H_{36}O_2$	C18:1
Methyl octadeca*dien*oate (linoleate)	$C_{19}H_{34}O_2$	C18:2
Methyl octadeca*trien*oate (linolenate)	$C_{19}H_{32}O_2$	C18:3

In addition to the FAME in table 2 one more was used; deuterated methyl heptadecanoate, d33. It was used as an internal standard. However, it took some time for d33 to arrive at Volvo and up until then tetradecane and eicosane were used as internal standard substitutes for the non-polar application and none in the polar application. Unless stated otherwise, d33 was used.

Included in **IP 585** is a sampling procedure, the procedure is described and carried out in accordance with another standard, **IP 475**.

The Gas chromatograph used was Agilent Technologies 7890B GC System equipped with a HP-INNOWAX 19091N-205I column and an auto-sampler. It was combined with an Agilent Technologies 5977B MSD. Since Volvo was interested in assessing the possibility of adjusting the method to a non-polar column. Since the polar column had not arrived at the company at the start of this thesis work, an experiment trying to get the method to work with a non-polar column at the start was warried out. For this experiment, the polar column was switched with the non-polar column 19091S-433UI. Heptane and chloroform were used instead of hexane.

2 Method

2.1 Adjusting IP 585 to a Non-polar Column

The testing performed on the non-polar column was based on IP 585 and initially the method was run on the column as is in scan mode, with the exception that solvent delay was set to 4 min, with the external standard as samples. After looking at the spectra and comparing them with each other it was realized that the separation was sub optimal because of the high temperature of the IP 585 standard's oven configuration and the column being overloaded because of the split-less injection. Thus, the initial temperature was decreased and the temperature increase over time was reduced and split set to 50:1, the samples were then re-run. After the re-run the separation was much better, it was then realized that the different FAME all had elution times between 20-28 min and thus the oven program was shortened to 28 min. The solvent delay was increased to 14 min since tetradecane eluted at 14.5 min. There seemed to be other substances eluting at a similar time and thus the concentration of the internal standard was evaluated. At this point in the project the polar column arrived and therefore testing was discontinued.

2.2 IP 585 on the Polar Column

Initially the column was prepared, put in place and then "baked" (run at the max temperature for a longer amount of time) for 6 hours. After baking the column some empty and some solvent sample runs were carried out. First two heptane samples were run, then two empty runs that showed that the heptane didn't leave the column right away. After discovering this, chloroform samples were run to remove it from the column. At least two runs with chloroform were run after each sample.

Preparations of standard solutions were carried out in accordance with IP 585. Two kinds of solutions were made with gasoline (to begin with) in the preparation: an internal standard solution which contained deuterated methyl heptadecanoate (methyl margarate-d33) and external standard solutions with different concentrations. The concentration ranged from 0 to 100 mg/kg. The external standards were made by first preparing a "bulk calibration solution" which contained 1 000 mg/L of each FAME in gasoline. From the bulk solution a "working standard solution" was made which then was used to prepare the final working calibration standard solutions. Here an internal standard made from gasoline and tetradecane was made. Then 10 µl of the internal standard solution was added to the working calibration standard solutions. After external standard solutions were made they were put in a fridge for storage. All samples and solutions were stored at approximately 4-5 °C when not in use. The second time the standards were made, they were made with dodecane instead of gasoline.

One milliliter of a sample supposedly containing FAME was added to a glass vial, 10 µl of internal standard solution was added. The cap was then put in place and the vial was shaken for approximately 3 seconds.

The first samples run after cleaning the column were the same external standard samples that were analyzed with the non-polar column in scan mode. With the retention times estimated from the first set of runs the SIM method was made. It was then validated by running the old standards once again. Once the peaks were not cut off by the different "scan windows", the ion dwell times were tweaked. When the method was complete, the GC was prepared to

analyze the new standard samples. It was noted that samples containing higher concentration of FAME required more post sample cleaning before the column was clean enough for the next concentration. At least 3 washes with cyclohexane was required for concentrations above 40 mg/kg.

To verify the method, samples were also sent to an external lab for comparison in a round-robin study. These samples were made with RME only and prepared by first preparing a solution containing approximately 100 mg/kg of RME. 0.1 g of RME was added to a round flask put on a scale which was then filled with gasoline until the total weight was 10 g. Then 1 g of the prepared solution was taken and added to another round flask which was then filled to 100 g with gasoline. The concentrations prepared were 5, 10, 25, 50, 75 and 100 mg/kg. This was done volumetrically. The sample's that were sent were supposed to contain 5, 50 and 100 mg/kg RME.

When the second batch of samples had returned, the standards were remade with dodecane and now also with d33 as internal standard. This internal standard was made by rinsing the vial that contained d33 with dodecane and decanting it into a 25 ml volumetric flask. After the vial had been rinsed around seven times, the rest of the volumetric flask was filled directly with dodecane. The external standards were made in the same way as before.

2.3 Sample testing

First the external standard solutions were analyzed, and Excel was used to create a calibration curve, thoroughly explained in part 2.4. After the calibration was made, the samples were put in the auto sampler and run according to IP 585. Heptane was used for syringe washing and put into its specific place. Every 5 samples the 2 mg/kg standard was run to confirm that the quality of the results stayed the same. If the difference between the previous standard run exceeded 5% the last 5 samples were discarded and analyzed again using the new calibration.

2.4 SIM Data Handling

2.4.1 Without Internal Standard

First the results from all external standards were gathered and used to plot concentration over peak-area in a data processing program. A calibration curve forced through zero was created by regression analysis. With help from the software the calibration curve’s equation was acquired. This equation was then used to determine the concentration of FAME in unknown samples by inserting the area of each peak in to each corresponding equation.

The peaks were distinguished visually in the TIC, time data from the standard runs were used as reference. Peak areas were then inserted in the external standard's concentration equation and the concentration was determined. This was repeated for all FAME. The individual concentrations were then summed together to retrieve the total concentration of FAME.

2.4.2 With Internal Standard

The area of all peaks in the sample were gathered and exported to Excel. All FAME’s areas were divided by the area of the internal standard of that sample. The actual concentrations from the dilution of the calibration samples were plotted over this ratio, called R. A calibration curve was made and its equation was retrieved. This was repeated for all FAME

just as in the previous segment. The difference being that the ratio R is used to determine the concentration instead of pure peak-area. When the concentration FAME has been determined in a sample, it is rounded to the closest 0.1 ppm all according to IP 585, and then presented in a table.

3 Results

3.1 Non-polar Column

It was noted that the separation of C18:1-3 was bad in comparison with the other FAME. They were never fully separated and the C18:3 peak was never discovered. The time was measured at the center of the peaks in the TIC.

Table 3: Approximate retention times measured.

FAME	Approximate Retention Time (minutes)
Palmitate C16:0	20.8
Margarate C17:0	22.7
Stearate C18:0	25.2
Oleate C18:1	24.5
Linoleate C18:2	24.3
Linolenate C18:3	---*

*C18:3 was never isolated.

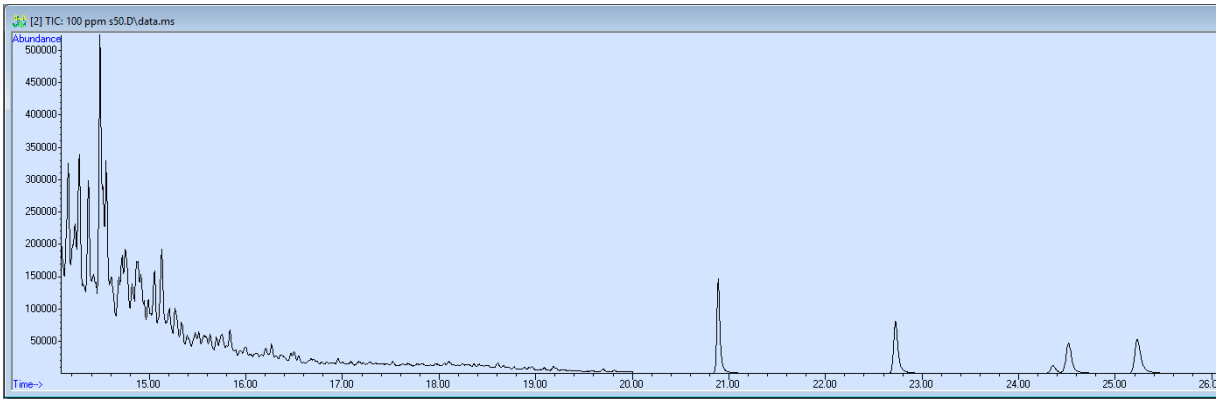

Figure 3: TIC from 100 ppm in gasoline, no internal standard.

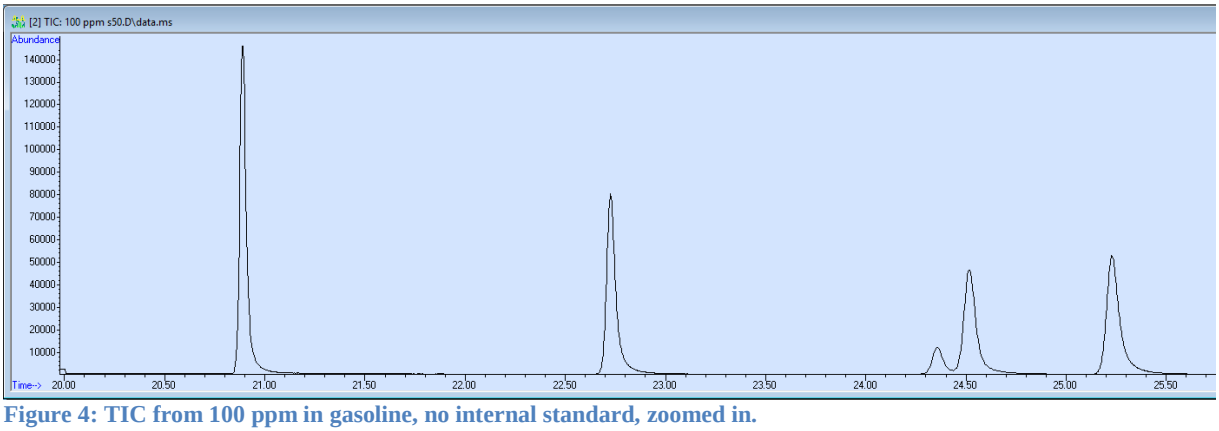

Figure 4: TIC from 100 ppm in gasoline, no internal standard, zoomed in.

3.2 Polar Column

Table 4: Approximate retention times measured.

FAME	Approximate Retention Time (minutes)
Palmitate C16:0	22.4
Margarate C17:0 d33	26.0
Margarate C17:0	28.0
Stearate C18:0	32.45
Oleate C18:1	33.8; 34.2*
Linoleate C18:2	35.9
Linolenate C18:3	38.25

*When the cis- and trans-isomers of C18:1 appeared as separate peaks.

In table 4, the time was measured at the center of the peaks in the TIC.

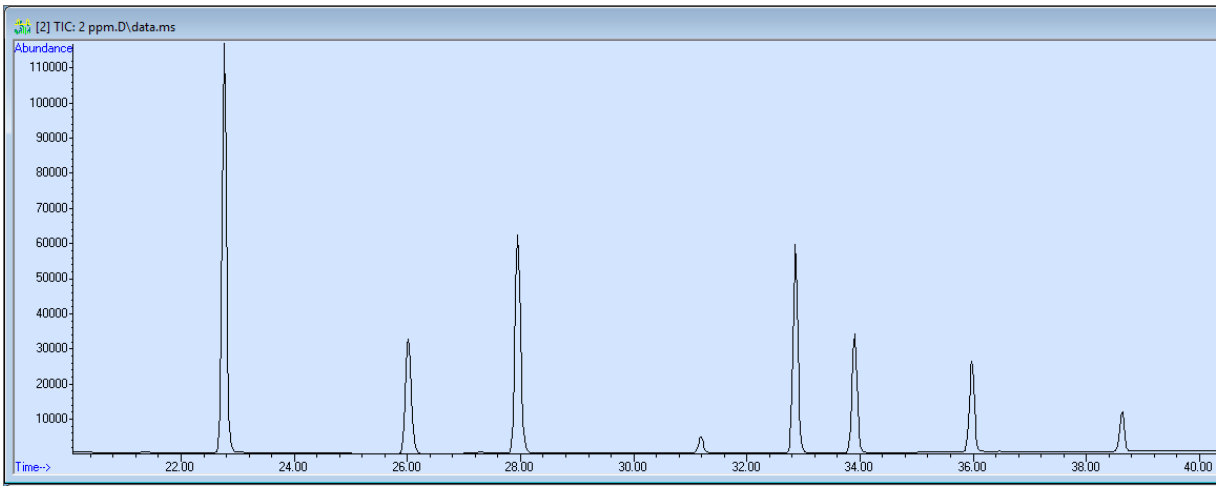

Figure 5: TIC from calibration series, 2 ppm in dodecane.

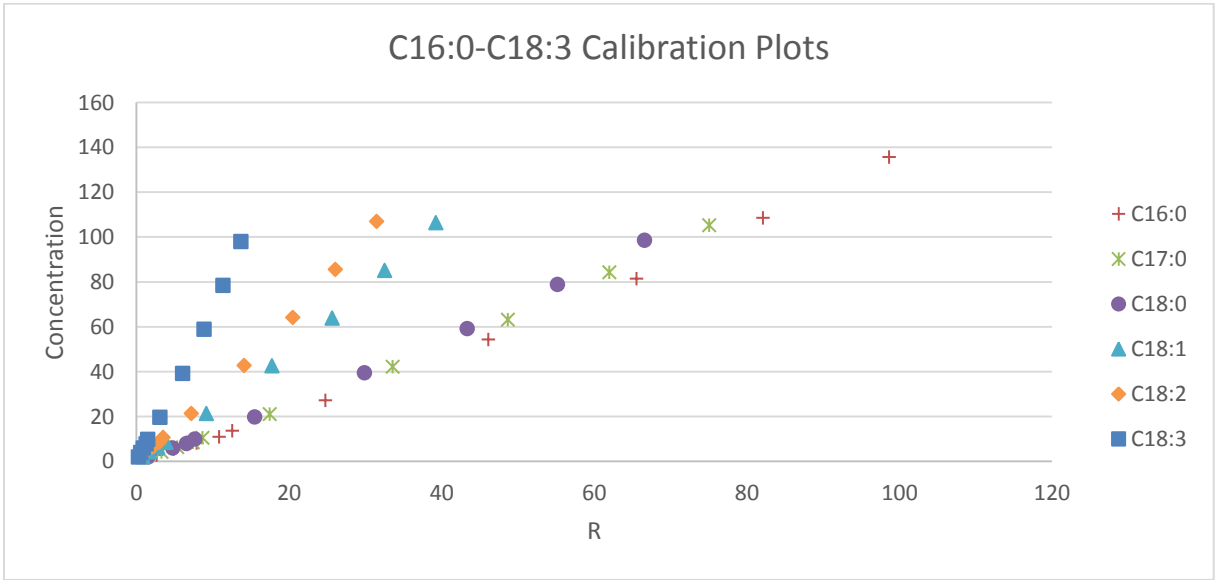

Figure 6 – Calibration made with internal standard

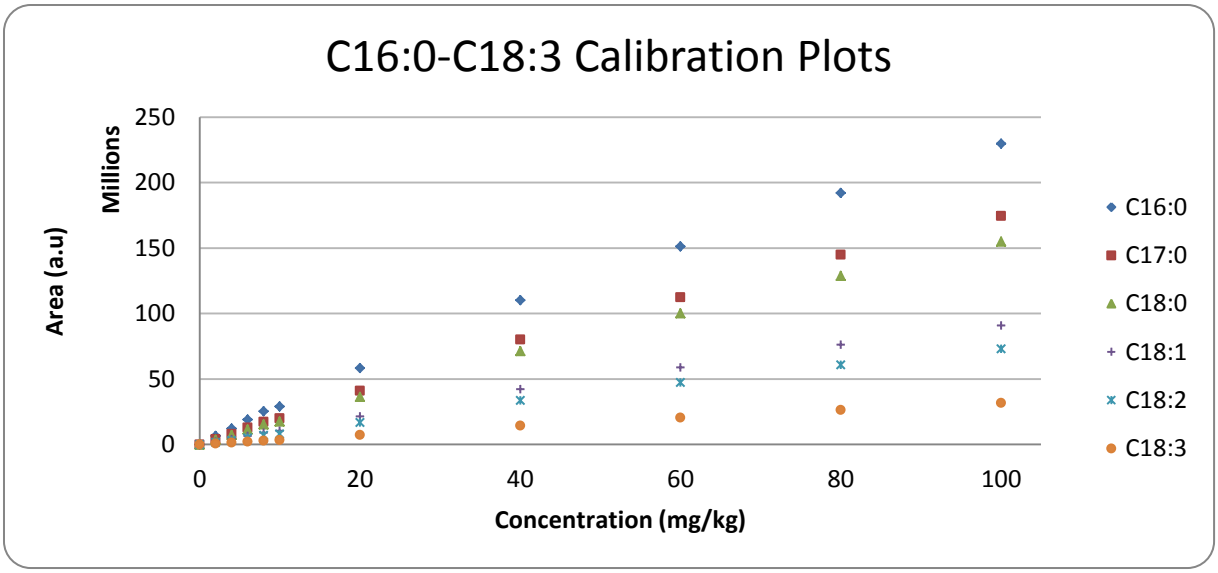

Figure 7: Calibration made without internal standard

Figure 7 shows the area received from the GC-MS integration software plotted over calculated concentration. One example of calibration curve when not using d33 is found below, the rest can be found in appendix A.

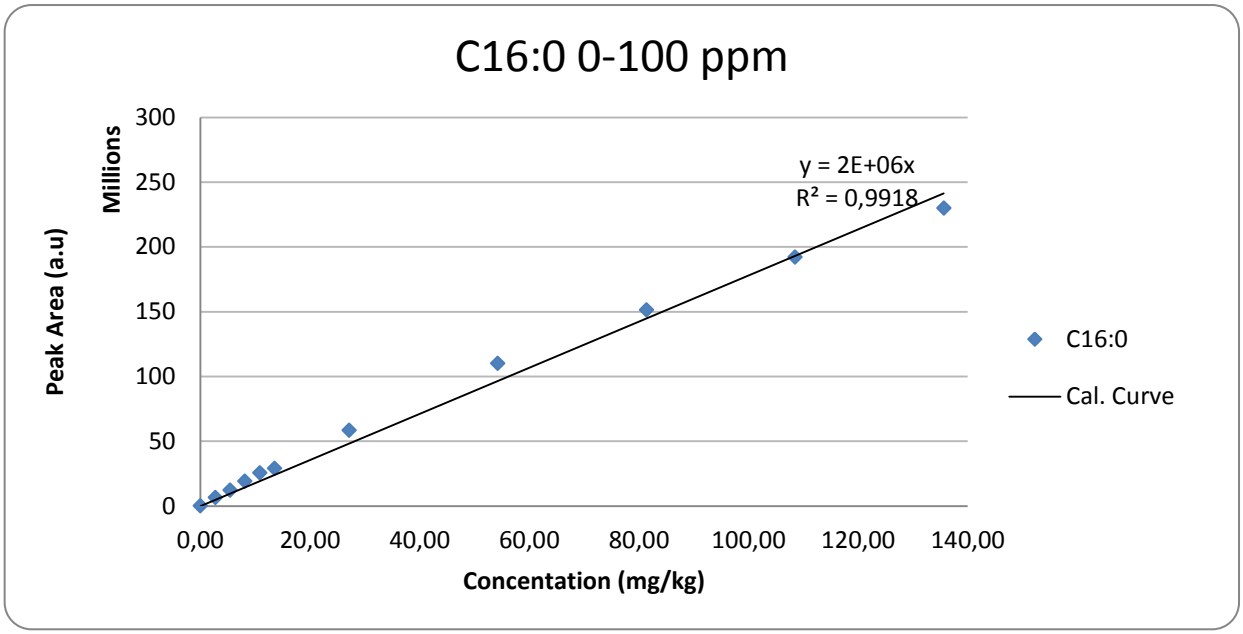

Figure 8: Calibration curve for methyl palmitate from 0-100 ppm FAME.

To clarify: All samples named "Sample X" are made from the flask named "Sample X". In other words, they are samples taken from the same flasks but not necessary from the same vials.

Table 5: Sample Results from GC-MS, gasoline calibration series.

Samples made without internal standard	Assumed Concentration (mg/kg)	From GC-MS (mg/kg)
98 CERT T-2, 180124	< 2	--
Sample 1	5	5.0
Sample 4	50	45
Sample 7	100	88

Table 5's results are derived from the first calibration made.

Table 6: Sample Results from GC-MS, gasoline calibration series.

Samples made without internal standard	Assumed Concentration (mg/kg)	From GC-MS (mg/kg)
98 CERT T-2, 180124	< 2	2.1
Sample 1	5	0
Sample 4	50	14
Sample 7	100	30

Table 6 includes the same sample-vials as table 5 but re-run after standards made of dodecane and FAME. The concentrations were measured without internal standard as reference.

Table 7: Sample results from GC-MS, first dodecane calibration series.

Samples made with internal standard	Assumed Concentration (mg/kg)	From GC-MS (mg/kg)
Sample 1	5	5.0
Sample 4	50	52
Sample 7	100	96

The samples in table 7 was run directly after the dodecane and internal standard calibration standards were run.

Table 8: First run of Sample 1, 4, 7. Sample results from GC-MS, first dodecane calibration series.

Samples made with internal standard	Assumed Conc. (mg/kg)	From GC-MS (mg/kg)	Standard Deviation (%)
Sample 1 I	5	6.2	
Sample 1 II	5	6.0	
Sample 1 III	5	7.0	
Sample 1 average	-	6.4	±8
Sample 4 I	50	50	
Sample 4 II	50	54	
Sample 4 III	50	46	
Sample 4 average	-	50	±8
Sample 7 I	100	92	
Sample 7 II	100	105	
Sample 7 III	100	117	
Sample 7 average	-	105	±12

Samples in table 8 were made at the same time in the same manner, but in different vials resulting in 3 vials for each sample.

Table 9: Second run of 1, 4, 7, new vials. Sample results from GC-MS, first dodecane calibration series.

Samples made with internal standard	**Assumed Conc. (mg/kg)**	**From GC-MS (mg/kg)**	**Standard Deviation (%)**
Sample 1 I2	5	7.1	
Sample 1 II2	5	7.7	
Sample 1 III2	5	7.4	
Sample 1 Average	-	7.3	±3
Sample 4 I2	50	54	
Sample 4 II2	50	*35.0	
Sample 4 III2	50	55	
Sample 4 Average	-	48	±21
Sample 7 I2	100	94	
Sample 7 II2	100	109	
Sample 7 III2	100	103	
Sample 7 Average	-	102	±7

Samples in table 9 were made at the same time in the same manner, but in different vials resulting in 3 vials for each sample.

3.3 External Lab Results

Table 10: The results achieved by the external lab.

Sample Name	**Assumed Concentration (mg/kg)**	**External Lab (mg/kg)**
98 CERT T-2, 180124	< 2	< 4.5 (1.7) *
Sample 1	5	< 4.5 (1.3) *
Sample 4	50	11.2
Sample 7	100	26.5

*If the concentration was lower than 4.5 mg/kg the external lab would answer < 4.5 and the concentration measured inside brackets.

4 Discussion

4.1 Method Discussion

The standard method IP 585 was well described and easy to follow. However, when looking into it there are parts that could be adjusted or at least clarified. To begin with, it is not necessary to make 100 ml of internal standard solution if the same precision is kept when making other quantities. Since only 10 µl of ISS is used for each sample, there is a risk of preparing too much solution which will start decomposing before it is used up.

As mentioned earlier, gasoline was used when preparing the external standard solutions instead of dodecane. This might have been overly ambitious and led to unnecessary difficult weighing problems since dodecane is less volatile than gasoline. The standard method could have been followed as is in that regard. This is why the standards were made with dodecane the second time they were made.

The measuring uncertainty can be reduced a bit since the use of an internal standard makes it possible to compare all peaks in every sample with a similar component in the standard, and then use that ratio between the internal standard peak in the sample and in the calibration curves to calculate the instrument's effect on peak area. As can be seen in the polar application method notes, no internal standard was used while calculating the concentrations to begin with. This was because it did not arrive on time when ordered. However, the concentration calculations are still valid but maybe not be as accurate. The use of an internal standard may be necessary if there is a demand on very high accuracy and to easily discover instrument induced faults.

When it comes to data processing and setting up quantification, if Excel or similar programs are used for creating the calibration curves, it might become ineffective since a lot of information needs to be processed. In addition to this, there are a lot of steps to follow and many ways to make mistakes. To reduce this risk, it is probably a good idea to use a program made for making calibration curves and quantification, such as “Quant My Way” integrated in Agilent’s GC-MS control software.

4.2 Result Discussion

When comparing the peaks from the polar with the non-polar column, it is clear that the peaks at low concentration from the polar column still look like peaks, instead of the bump-like shapes from the non-polar column. This can be seen in the images below where two samples at the same concentration have been analyzed with the non-polar and polar column.

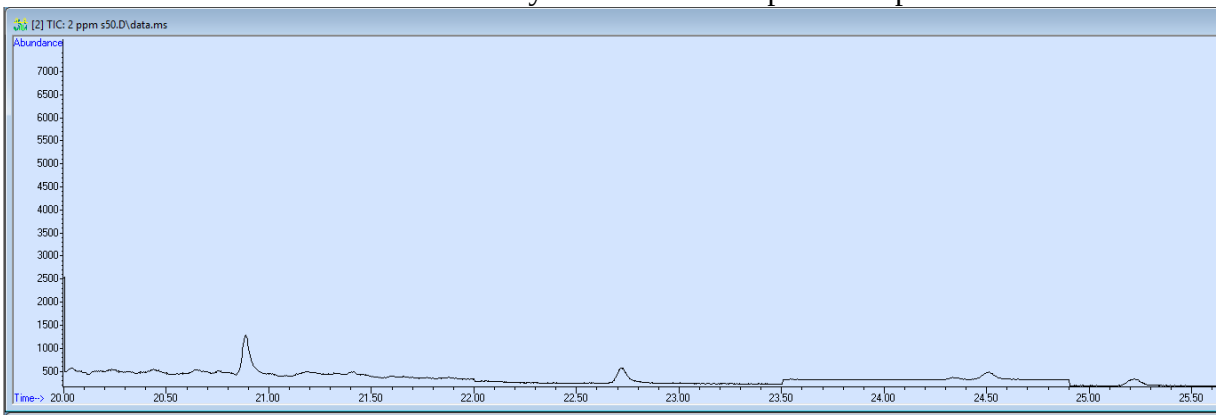

Figure 9: TIC from non-polar column at 2 ppm.

Fig 8 is from the non-polar column and it is as mentioned above the same concentration as in fig 9, but the peaks look nothing like each other. This is the case for lower concentrations of FAME. Just the way they look is an argument for the polar column to be used instead. In addition to this, look at the abundance; the amplitude is much higher with the polar column. Not to mention the resolution.

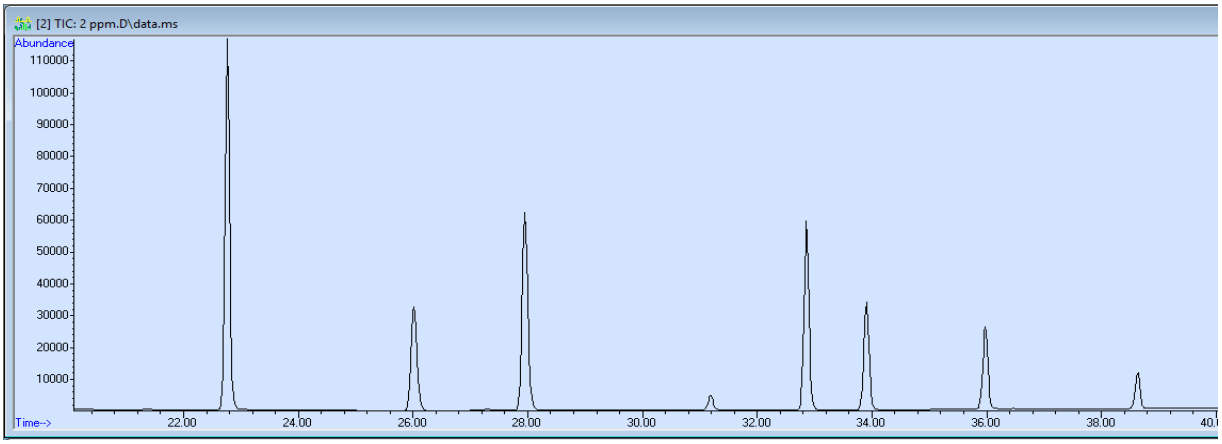

Figure 10: TIC from polar column 2 ppm.

The amplitude does increase for the non-polar column as well and it would probably be possible to use the non-polar column for determination, at least at higher concentration or just as an indication in which range the concentration of FAME lies. Seen below is the results from 10 ppm analyzed in the non-polar column.

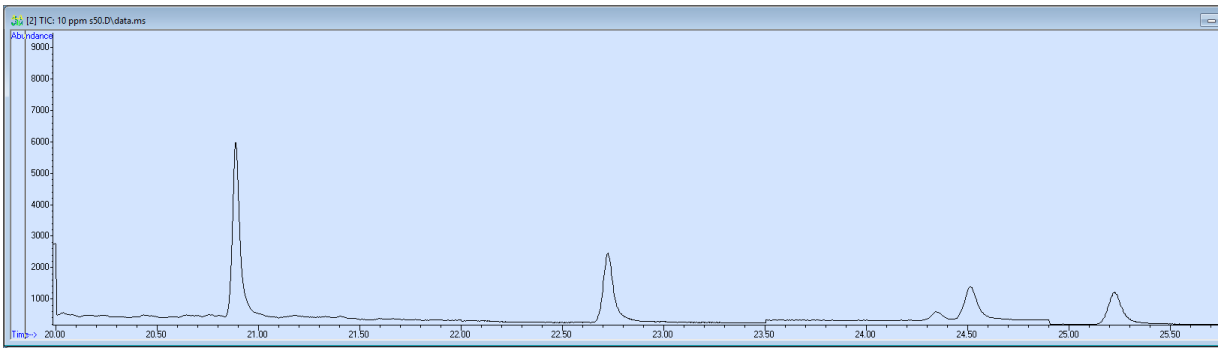

Figure 11: TIC from non-polar column 10 ppm.

As stated in the results, C18:1-3 was never fully separated in the non-polar column. A possible reason for this is that they have a too similar affinity to the column's stationary phase in comparison to the column length and oven program temperature. The C18:3-peak has probably merged with either the 18:2 or 18:1 -peak. If the retention time of C18:3 is affected in the same way as C18:1-2 then it should be seen at 24.1 min. In the image below, you can see that there are only two peaks in the nearby area where C18:1-3 should have been. The peak to the left is C18:2 and the peak to the right is C18:1.

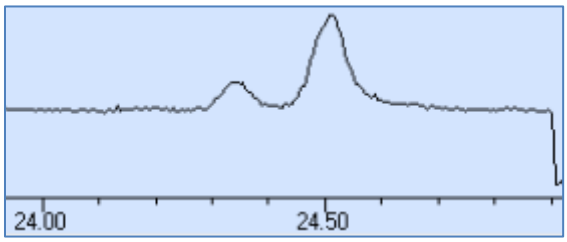

Figure 12: Zoom in on a 2 ppm peak at the C18:1-3 time segment.

It was discovered that the elution order was different for the two columns. The difference being that C18:0 to C18:3 eluted in opposite order.

When it comes to the answers from the external lab, the numbers does not add up. There was an instance, as seen in table 8, where similar numbers were retrieved from the GC here at Volvo. It was only that time those numbers were retrieved and it was not possible to recreate that scenario later on when following IP 585 as is.

There are two samples that had a concentration below 4.5 mg/kg as can be seen in table 8. When analyzing the results, it should be taken in consideration that any answer below 4.5 mg/kg is outside the defined range of the method and the result might not be as accurate as the ones within.

To compare the peaks from the polar column with the non-polar column, there are several differences. Peak width, peak height and peak intensity are variables that tend to behave differently for the same concentration in the two columns. There could be several explanations for this behavior. The most obvious are column affinity and length. But temperature gradient and injection volume could also be one of many factors that affect the look of the peaks.

It was noticed that the calibration curves seemed to not be linear. If studied closely it looks like the instrument response is not as linear as stated in IP 585. This behavior is inversed for the concentration over R calibration curves but it still follows the same pattern. It looks like the calibration curves can be approximated more accurately with a $\sqrt{x}$ –function. This is however not mentioned in the standard method IP 585 and might therefore be something that needs to be investigated further.

4.3 Problem Factors and General Issues

When weighing FAME and gasoline in the making of standard solutions it was noted that the solution was volatile enough to prevent the scale from staying at one weight. The third decimal (0.001 g), was constantly decreasing. This made it difficult to keep the measurements accurate, especially at low concentrations where both precision and adding one drop at the time was necessary. To reduce evaporation, narrow neck flasks were used as much as possible and cap locked tight as often as possible.

In addition to difficulties in being precise when weighing gasoline, it was also difficult when handling it volumetrically. The low surface tension made the pipette drip. To reduce this, a pipette with a longer and thinner tip was connected to the tip of the auto-pipette with a small silicon tube. It did reduce the dripping significantly. However, it was still difficult to keep the measuring procedure the same for all iterations.

After installing the new column, the base line started to behave different from earlier runs. It was not consistent and changing over time. After tightening the septum, the problem seemed to have been solved. It disappeared for 3 weeks before getting discovered again. When it returned for the second time, a more in-depth troubleshooting session was initiated. This problem disappeared after changing septum and liner. The glass wool of the liner had moved from one end to the other.

4.4 Continued Research

To proceed in adjusting the method to a non-polar column, an internal standard that won't elute at the same time as the other components in the sample would be to prefer. Tetradecane elutes at approximately 14 minutes with the column used, a lot of other components in gasoline elute at the same time and it can therefore not be excluded that they do not interfere with the tetradecane-peak. This becomes a problem when testing gasoline made at different times of the year, but also when trying to create a method for both 98 and 95 octane gasoline. A possible workaround could be using eicosane.

Take note that all FAME solutions should be used within 3 months according to IP 585. This does also apply to d33 and might therefore be one of the reasons for this method to become expensive if not enough samples are run at the given time interval or measures are taken to reduce the usage of d33. The recipe of the internal standard is for making 100 ml. Testing samples only require 10 µl per sample and 100 µl in the making of external standards. One idea that came up while making the standard, other than mixing a smaller volume, is that it might be possible to use a different concentration than the one stated in the standard. For as long as the concentration of the internal standard is the same in both the samples and the

external standards, it should not matter what concentration of d33 is used for as long as the peak is well defined.

There must be other substances that can be used as internal standard instead of d33 in both the polar and the non-polar application. Since the main part of the sample is gasoline and the substances looked for are very well defined, it should be possible to find a working substitute just by testing different substances in the column which preferably is different from gasoline but also different from the FAME. If no other eligible substitute is found it might be a good idea to try to use one of the FAME C16:0-18:3. Since it is known what oils are used to produce FAME in Sweden; pick a FAME such as C17:0 which does not exist in RME. It does make the method incompatible with global gasoline samples that might contain that specific FAME though. To save some trouble it might be possible to use the changed method at Volvo for analysis of samples with gasoline made in Sweden but sending the samples of gasoline collected outside of Sweden to be analyzed externally. A possible work around would be to start the sample testing by screening the samples without adding an internal standard just to verify that the sample does not contain the FAME that is being used as the internal standard. Two other possible substitutes might be nonadecanoic acid methyl ester or maybe a fatty acid ethyl ester.

Use dodecane instead of gasoline when creating the external standards. It is much easier to work with in comparison with gasoline. Even when working in a fume hood you will most likely get in contact with the fumes in one way or another. Aside from the fumes, all other problems that comes with weighing or measuring gasoline volumetrically disappears.

It seemed possible to adjust the method to a non-polar column, but the adjustments were never finished: The method oven program for the non-polar column might need to be re-evaluated, it is set to be as short as possible and this might be too short if some parameter slows down the elution. The slowest eluting FAME left the column at approximately 25 minutes. Therefore, the program was set to end after 28 minutes for now. Also, if an internal standard which elutes later than 28 minutes is to be used, the program will definitely have to be changed.

5 Conclusions

It is possible to measure the FAME content in gasoline samples using a GC-MS with the method IP 585 within the range 4.5 to 150 mg/kg. The accuracy seems to vary depending on concentration level and there might be factors affecting the accuracy not mentioned in the method description IP 585. It was found out that there are alternatives available to IP 585 such as methods using EDXRF or FT-IR. It also seems possible to adjust IP 585 to a non-polar column. It might however not be possible to adjust it to have the same accuracy and resolution as on the polar column, since the peaks C18:1-3 seemed to have merged together, but none the less possible to use it. It could at the least be used for approximating FAME concentration.

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APPENDICES

Appendix A – Polar Calibration Curves and Equations

Curves and equations from using area

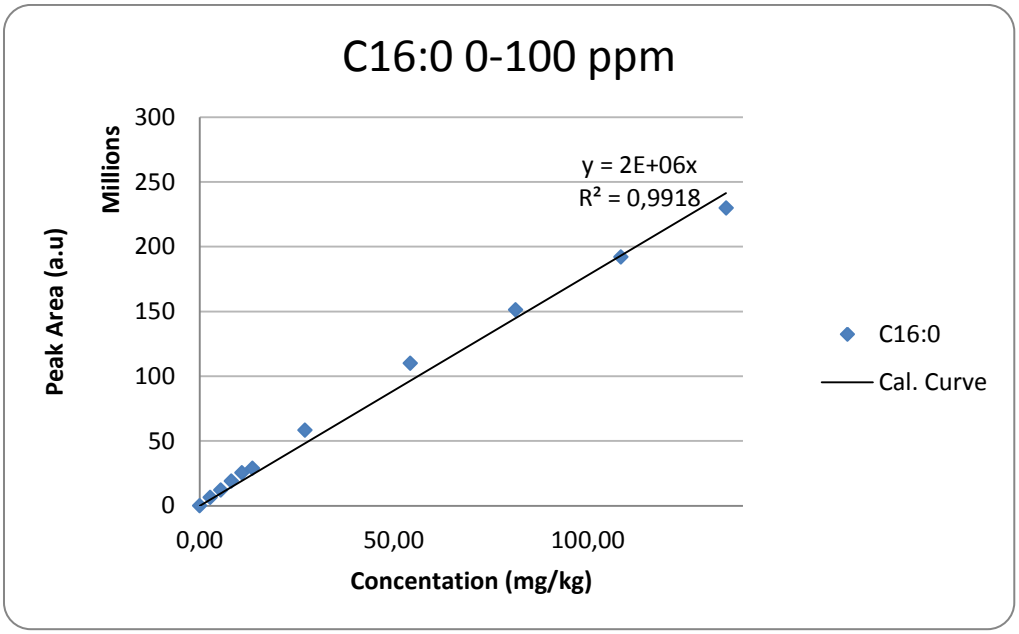

Figure 13: Methyl hexadecanoate calibration curve and plot.

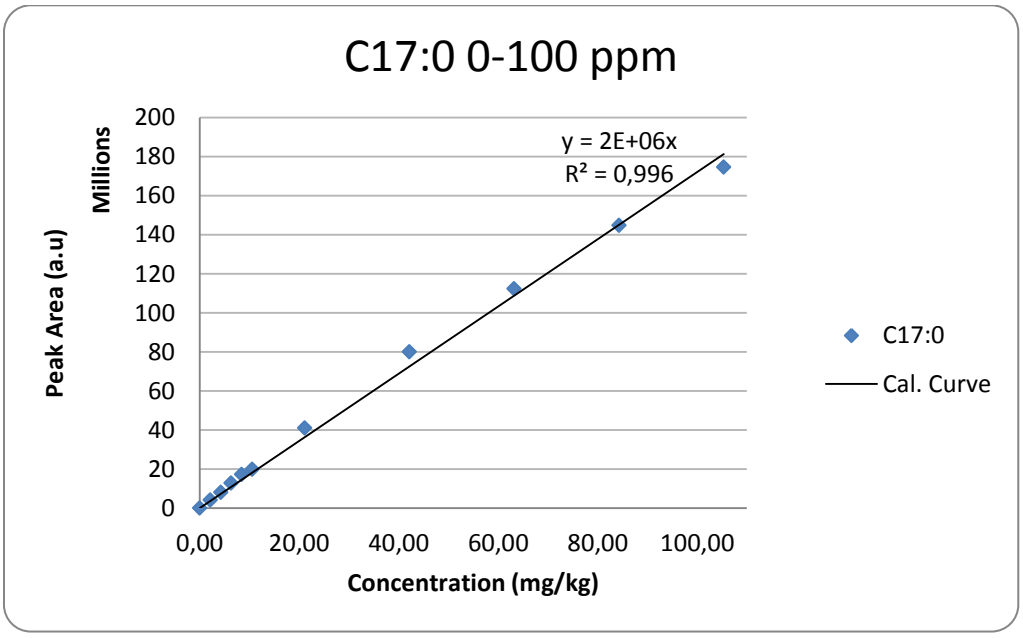

Figure 14: Methyl heptadecanoate calibration curve and plot.

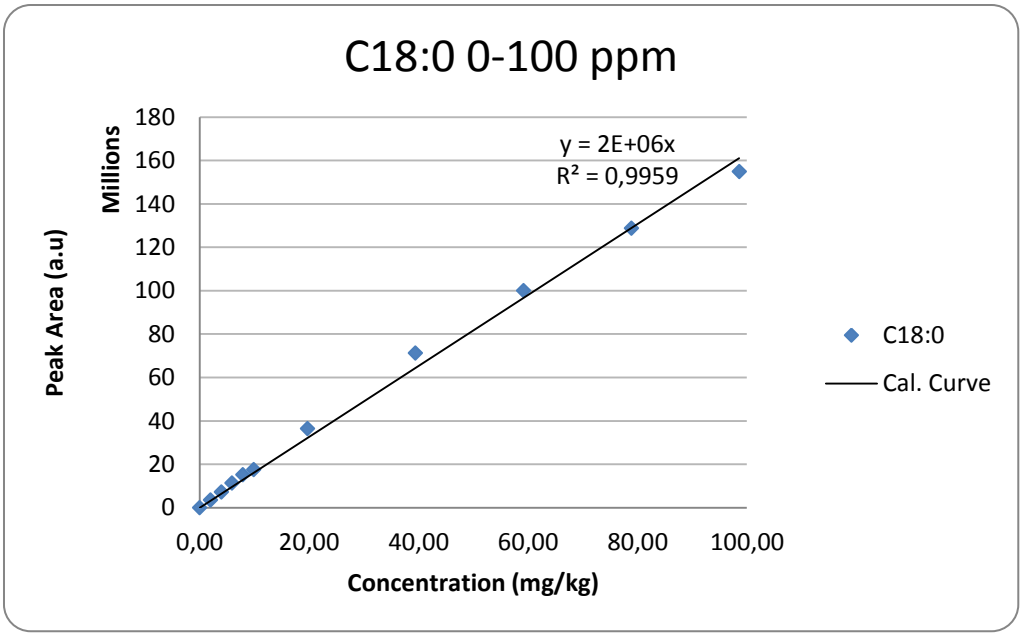

Figure 15: Methyl octadecanoate calibration curve and plot.

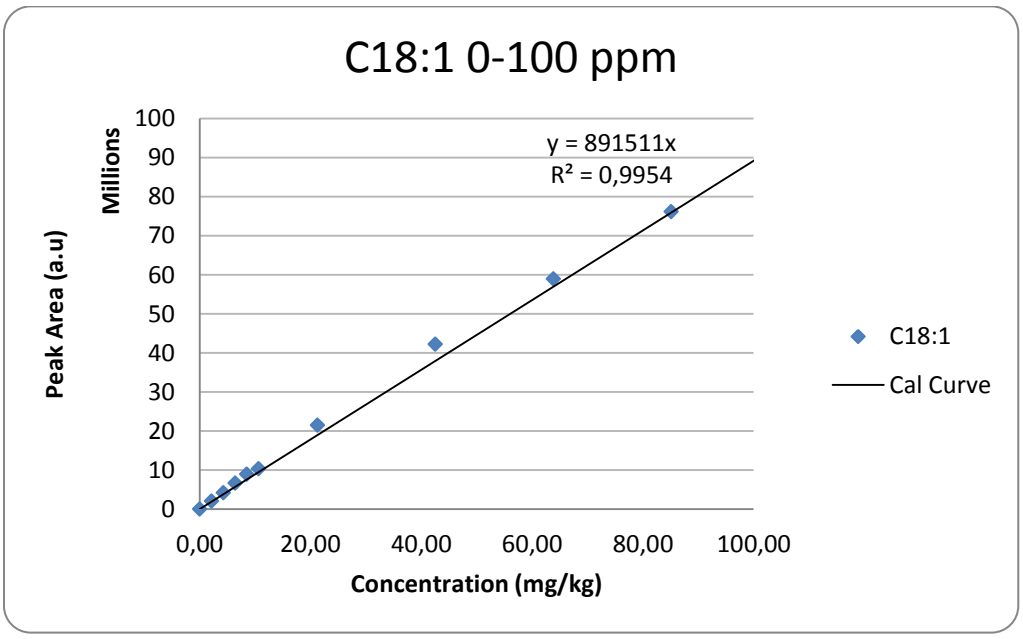

Figure 16: Methyl octadecenoate calibration curve and plot.

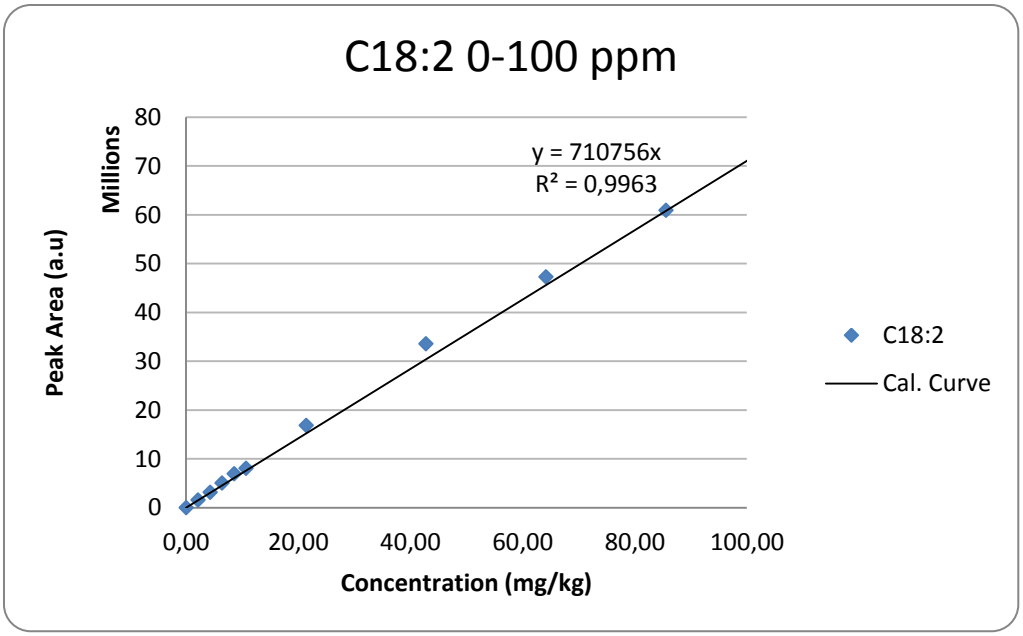

Figure 17: Methyl octadecadienoate calibration curve and plot.

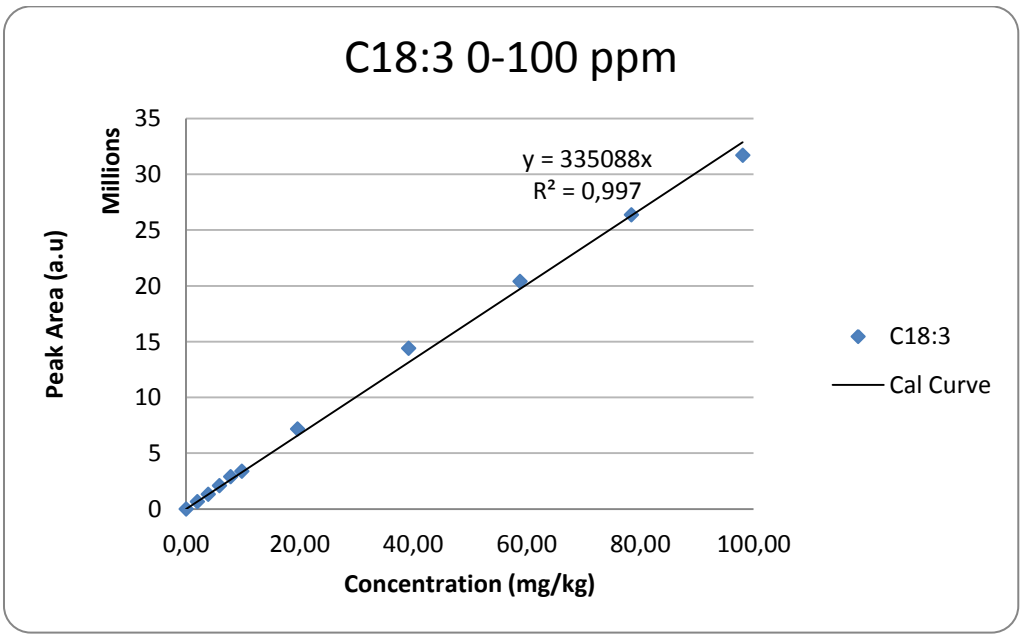

Figure 18: Methyl octadecatrienoate calibration curve and plot.

Table 11: Calibration equations from the dodecane with internal standard series, but using area.

FAME	Equation	R^2
C16:0	$y = 2 \cdot 10^6 x$	0,9918
C17:0	$y = 2 \cdot 10^6 x$	0,996
C18:0	$y = 2 \cdot 10^6 x$	0,9959
C18:1	y = 891511x	0,9954
C18:2	y = 710756x	0,9963
C18:3	y = 710756x	0,997

In table 10 Equation column: 'x' is the concentration FAME in mg/kg and 'y' is the peak's area.

Curves and Equations Using internal standard

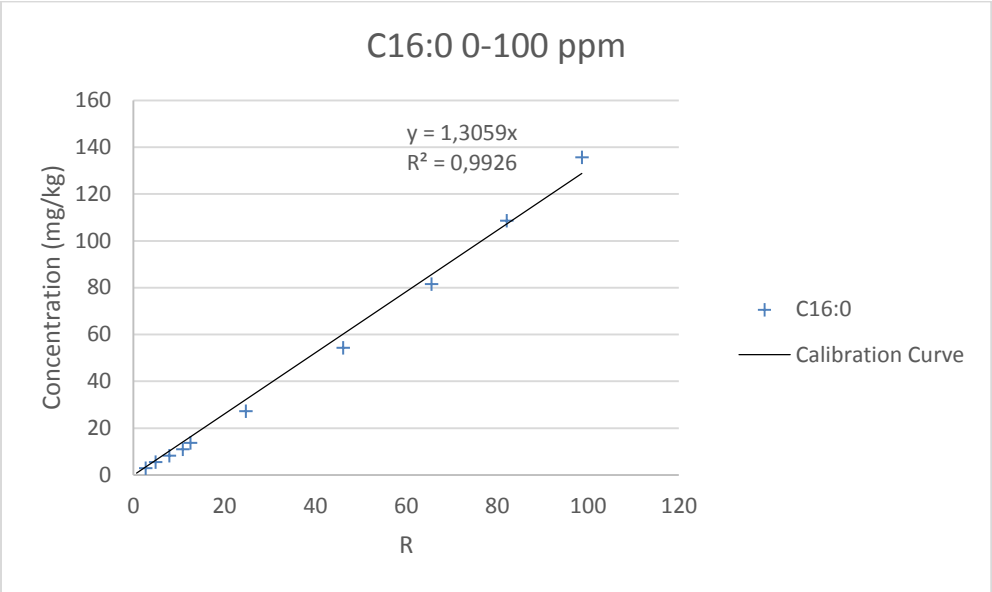

Figure 19: Methyl hexadecanoate calibration curve and plot. With internal standard as reference.

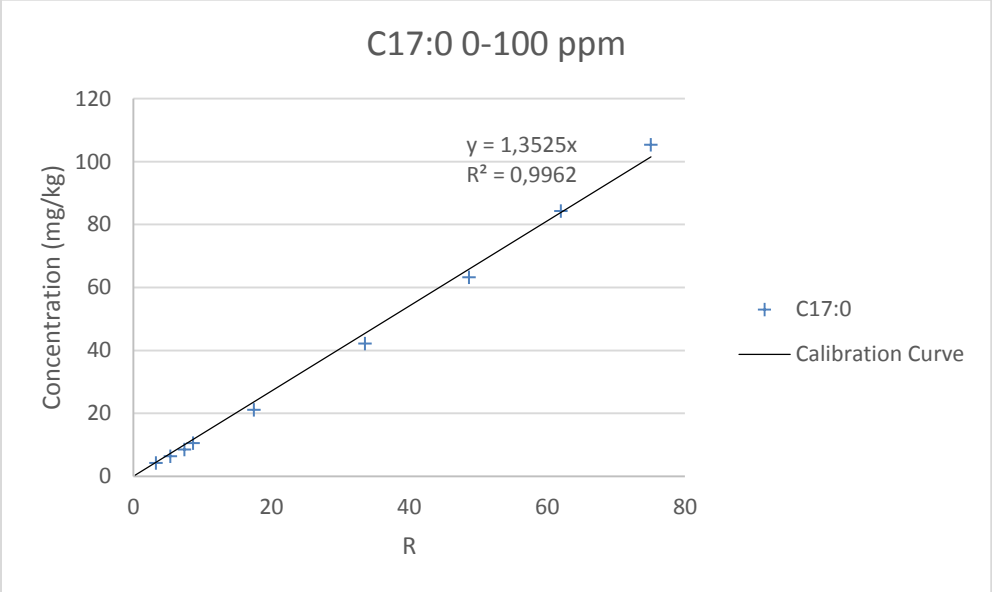

Figure 20: Methyl heptadecanoate calibration curve and plot. With internal standard as reference.

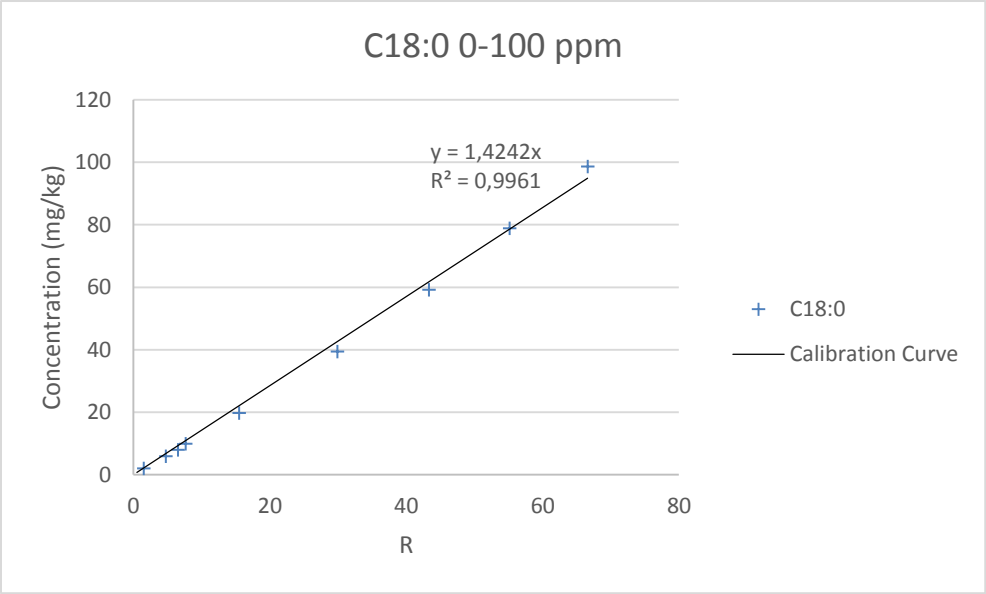

Figure 21: Methyl octadecanoate calibration curve and plot. With internal standard as reference.

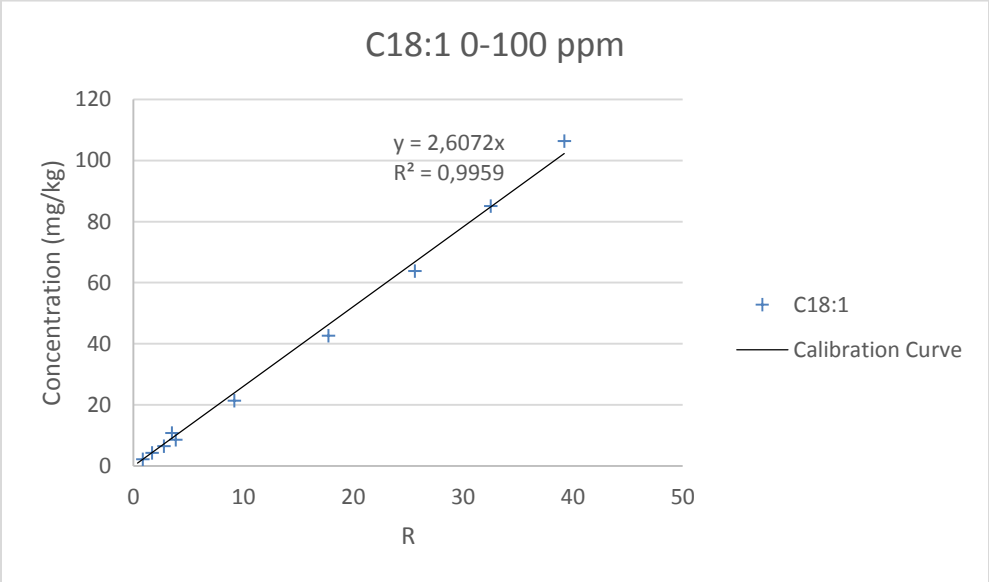

Figure 22: Methyl octadecenoate calibration curve and plot. With internal standard as reference.

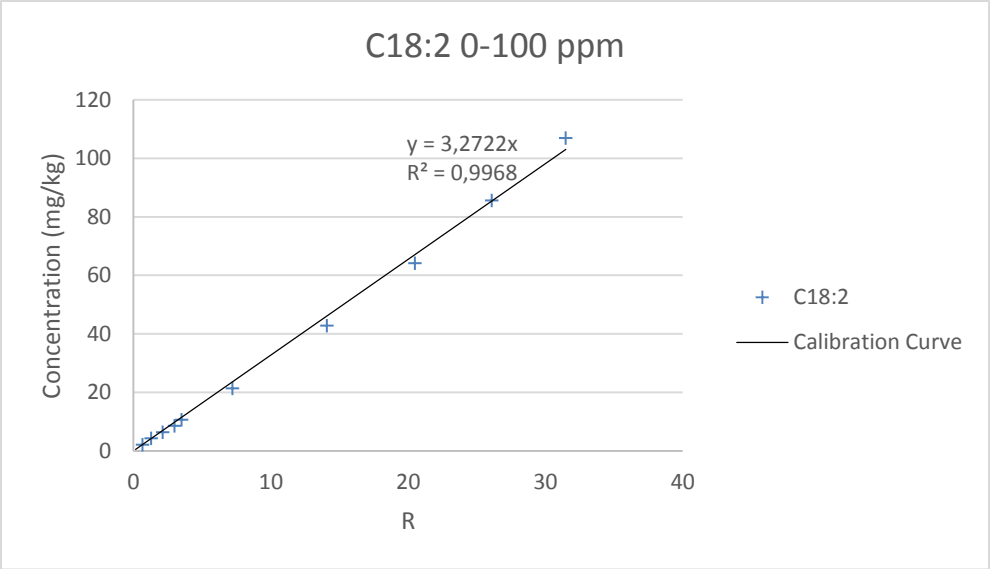

Figure 23: Methyl octadecadienoate calibration curve and plot

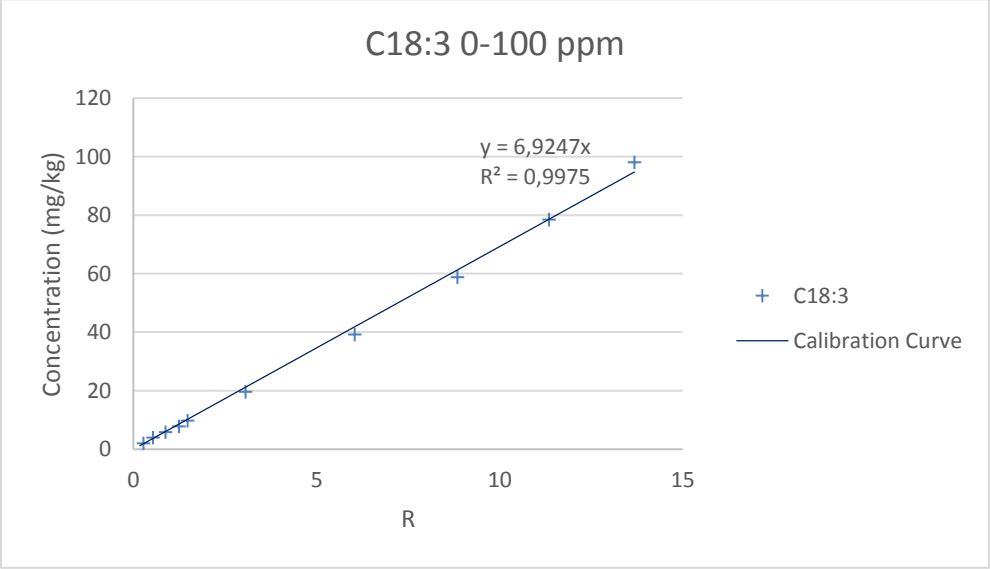

Figure 24: Methyl octadecatrienoate calibration curve and plot. With internal standard as reference.

Table 12: Calibration equations from the dodecane with internal standard series.

FAME	Calibration Equations	R^2
C16:0	y = 1,3059x	0,9926
C17:0	y = 1,3525x	0,9962
C18:0	y = 1,4242x	0,9961
C18:1	y = 2,6072x	0,9959
C18:2	y = 3,2722x	0,9968
C18:3	y = 6,9247x	0,9975

In table 11 Equation column: 'y' is the concentration FAME in mg/kg and 'x' is the ratio between the internal standard and FAME peak.

Appendix B – Ion Dwell Times Tweak TICs

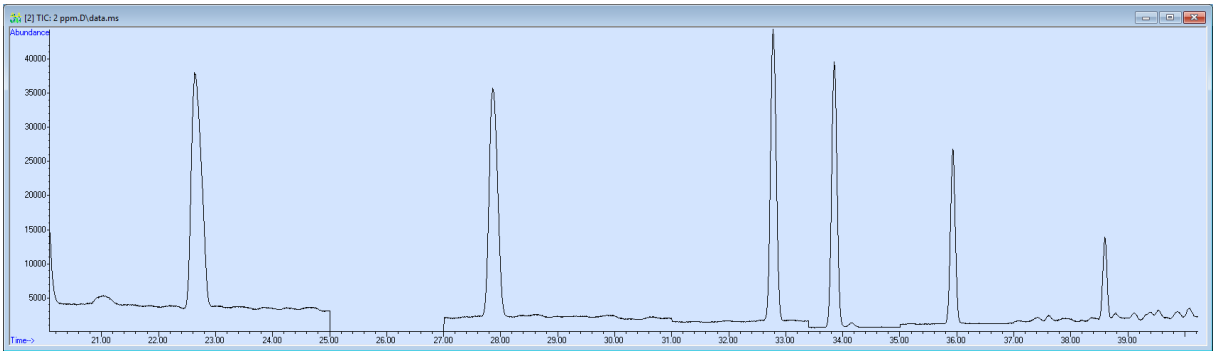

Figure 25: Original look of TIC.

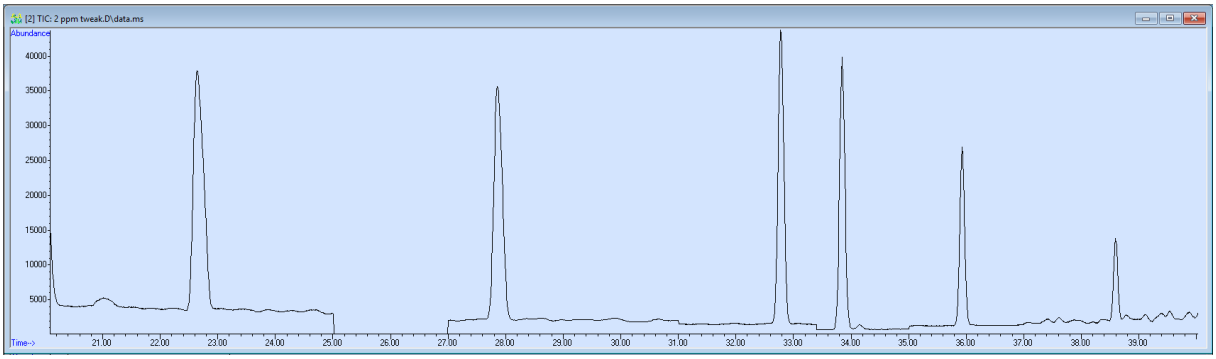

Figure 26: First tweak, more smooth baseline and peaks.

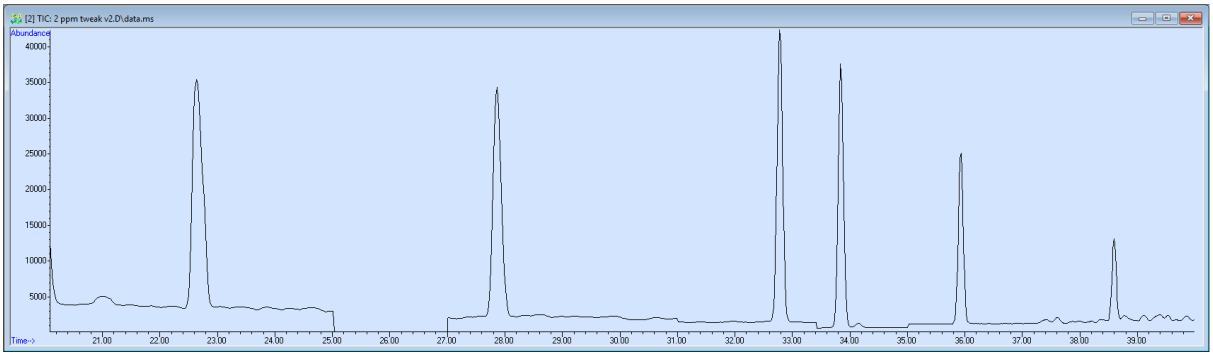

Figure 27: Final tweak, most even baseline and peaks.

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