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LSC Method Development for Measuring Changing Diesel Sample Matrix

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Abstract

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Neste Corporation is one of several oil companies that have proceeded to develop clean and long-term solutions to minimize CO_2 emissions. The quantity of renewable diesel in a fuel mixture may be determined using conventional analytical methods used to identify chemically different components using Liquid Scintillation Counting (LSC) and Accelerator Mass Spectrometry (AMS) to determine biogenic content. Biogenic proportion can be determined due to the decomposition of radiocarbon. Radiocarbon 14 (^{14}C) is a radioactive isotope of carbon that is unstable. The purpose of the thesis was to develop a method for the determination of the biogenic content of carbon using Liquid Scintillation Counter (LSC). The practical part of the thesis was performed in Neste Corporation's quality control laboratory in Porvoo.

A changing biobased sample matrix (CBM) was created containing fossil diesel, renewable diesel, and FAME biodiesel fuel, and 11 standard samples were prepared according to CBM series. Another 11 samples were prepared according to changing fossil matrix (CFM) containing renewable diesel, fossil diesel and fossil GTL fuel. Liquid scintillation cocktail was added to each sample in ratio 1:1. Each sample was then measured with the LSC, and biogenic carbon content calculated. A few samples from each series measured with liquid scintillation counter were sent to an external Helsinki University accelerator mass spectrometry (AMS) laboratory and these sample results were used as reference measurement. The validation parameters used were the linearity of the method and accuracy.

The method was determined to be suitable for biogenic content measurements of fuel containing 0-50 vol % of GTL and for fuel contain 0-5 vol % of FAME. It was realized by filtering color from FAME samples, color quench during measurement in LSC decrease.

Key words: liquid scintillation counter, biocontent, radiocarbon, FAME, renewable diesel.

Tiivistelmä

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Neste Oyj on yksi monista öljy-yhtiöistä, joka on siirtynyt kehittämään puhtaita ja pitkäaikaisia ratkaisuja hiilidioksidipäästöjen minimoimiseksi. Uusiutuvan dieselin määrä polttoaineseoksessa voidaan määrittää käyttämällä analyyttisiä menetelmiä, joilla tunnistetaan kemiallisesti erilaisia komponentteja käyttäen nestetuikelaskinta (LSC) ja kiihdytinmassaspektrometriaa (AMS) bio-osuuden määrittämiseen. Bio-osuus voidaan määrittää radiohiilen hajoamisen ansiosta. Radiohiili 14 (^{14}C) on hiilen radioaktiivinen isotooppi, joka on epästabiili. Opinnäytetyön tarkoitus oli menetelmän soveltuvuuden selvittäminen vaihtuvan dieselmatriisin näytteiden suhteen. Opinnäytetyön käytännön osa tehtiin Neste Oyj:n laadunvalvontalaboratoriossa Porvoossa.

Luotiin muuttuva biopohjainen näytematriisi (CBM), sisältäen fossiilista dieseliä, uusiutuvaa dieseliä ja FAME-biodieselpolttoainetta, ja valmistettiin 11 biopohjaista standardinäytettä CBM-sarjan mukaisesti. Toiset 11 näytettä valmistettiin muuttuvan fossiilisen matriisin (CFM) mukaan, joka sisälsi uusiutuvaa dieseliä, fossiilista dieseliä ja fossiilista GTL-polttoainetta. Jokaiseen näytteeseen lisättiin nestetuikeseosta suhteessa 1:1 ennen mittausta nestetuikelaskurilla. Menetelmällä määritetiin polttoainenäytteestä radiohiilen osuus ja sitä kautta laskettiin biopolttoaineen ja fossiilisen polttoaineen sekoitussuhteet. Jokaisesta nestetuikelaskurilla mitatusta sarjasta lähetettiin muutama näyte ulkoiseen Helsingin yliopiston kiihdytinmassaspektrometrian (AMS) laboratorioon ja näitä AMS:n näytetuloksia käytettiin vertailumittauksena. Käytetyt validointiparametrit olivat menetelmän lineaarisuus ja mittaustarkkuus.

Menetelmän todettiin soveltuvan 0–50 til.- % GTL: ää sisältävien polttoaineiden bio-osuuksien mittaamiseen. Menetelmän todettiin soveltuvan myös polttoaineille, jotka sisältävät 0–5 til.- % FAME: a.

Avainsanat: radiohiili, Uusiutuva diesel, nestetuikelaskuri, FAME, bio-osuus

Contents

List of Abbreviations

AMS Accelerator Mass Spectrometry

BGO Bismuth germanium oxide

CBM Changing biobased sample matrix

CFM Changing fossil sample matrix

CPM Counts per minute

DPM Disintegrations per minute

FAME Fatty acid mehtyl ester

HVO Hydrotreated Vegetable Oil

GHG Greenhouse gas

GTL Gas to liquid

LOD Limit of Detection.

LOD Limit of Detection.

LSC Liquid scintillation counter

m–% Percentage by weight.

NRD Neste renewable diesel

pMC Percent modern carbon

RSD Relative standard deviation

SD Standard deviation

tSIE Special Index of the Transformed External Standars Spectrum

1 Introduction

Global warming is widely acknowledged as one of the most pressing issues confronting our world today. Heat-trapping greenhouse gas levels are rising in the earth's atmosphere because of human activity. The daily actions of humans result in the release of greenhouse gases such as carbon and methane. These greenhouse gases restrict the earth's heat from escaping, resulting in global warming. The earth's global average temperature has risen by around 1 degree Celsius because of human activity, and it is now growing about 0.2 degree Celsius every decade. Fossil fuel combustion is the greatest source of greenhouse gas emissions caused by human activity [1]. Due to climate change the production and usage of sustainable and renewable energy has risen.

Neste Corporation is one of several oil companies that have proceeded to develop clean and long-term solutions to minimize CO_2 emissions. Neste is a top manufacturer of renewable diesel (Neste MY renewable diesel™) and sustainable aviation fuel produced from waste and residues across the world. Neste MY renewable diesel™ reduced greenhouse gas (GHG) emissions by 9,6 million tonnes in 2019 [2]. When compared to fossil diesel, it is created entirely of renewable raw resources and releases up to 90 % less greenhouse gas emissions over the fuel’s life cycle [3].

Both Neste Renewable Diesel and fossil diesel fuels include paraffinic hydrocarbons known as alkanes. Hydrocarbons of the paraffins (alkanes) family are completely hydrogen-saturated. These carbon skeletons have no double or triple bonds; therefore, they have the maximum number of covalent bonds between carbon and hydrogen [32]. The quantity of renewable diesel in a fuel mixture may be determined using conventional analytical methods used to identify chemically different components such as ethanol in gasoline or FAME (Fatty acid methyl ester) in diesel [4, p. 34].

The ^{14}C isotope method or radiocarbon dating method may be used to determine the amount of Neste Renewable Diesel in a fuel mix. This method is based on a ratio of stable ^{12}C and decaying ^{14}C carbon isotopes in the environment, which can be found in all living things. According to the half-life (5730 years), radiocarbon has already decayed in a fossil matter [Figure 4], which has been in na0ture for a long time, but in the new bio-based substance, the concentration of radiocarbon corresponds to the radiocarbon concentration of the atmosphere at that time [17]. Measuring and knowing the biogenic content is important, among other things, for the quality of renewable fuel. Biogenic content measurements ensure that the renewable content of a product defined as renewable meets the required values. Liquid scintillation counting (LSC), and accelerator mass spectrometry (AMS) are two widely accepted techniques for determining biogenic content. [4, p.34]

The purpose of the thesis was to develop a method for the determination of the biogenic content of carbon using a liquid scintillation counter (LSC) for samples of changing diesel-type matrix. The method determines the proportion of radiocarbon in a fuel sample thereby the blending rations of biofuel can be calculated. The method development investigates the applicability of the method to variable diesel matrix samples by making blending series and measuring Neste MY renewable diesel™, FAME biodiesel, fossil diesel and fossil GTL fuel. The practical part of the thesis was performed in Neste Corporation's quality control laboratory in Porvoo.

2 Different forms of biodiesel and their determination

2.1 Fatty Acid Methyl Ester (FAME) and Neste MY Renewable Diesel

Biodiesel is a diesel alternative mostly generated from recycled cooking oils although it may also be made from a variety of renewable and recyclable sources, including tallow

(animal) fats and plant oils. During the biodiesel generation process, these oils and fats are transformed into long chain molecules. Fatty Acid Methyl Esters is another term for these compounds, which are most often abbreviated "FAME" [21]. Fatty acid esters have physical properties similar to those of fossil diesel fuels; however, their characteristics vary according to the kind of vegetable oil. Biodiesel is a sustainable alternative fuel made of a blend of fatty acid methyl esters. Additionally, it is biodegradable and non-toxic. FAME contain also a strong dark brown color (Figure 12, p. 26)

When it comes to slowing down the oxidation process and ensuring correct low-temperature behaviour, biodiesel needs different additives than fossil fuel [22]. The loss of electrons by a molecule, atom, or ion during a process is known as oxidation. For usage as a motor fuel, the amount of metals in FAME must be reduced. Motor manufacturers in the European Union have conducted tests on diesel oil mixes ranging from 5% to 10%, or 25% to 30% and 100% pure. Each of them has resulted in a guarantee for that specific usage. Seals and pipework must be modified for usage in 100 percent pure solutions. Because no adjustments to the distribution system are necessary for the use of biodiesel as a low-blend component in transportation fuel (up to 7% in Europe for the time being according to EN 590), expensive infrastructure changes may be avoided [35]

FAME is produced through transesterification of vegetable oils, animal fats, and waste cooking oils. The transesterification reaction is a reversible reaction. In reaction shown below glyceride reacts with an alcohol in the presence of a catalyst to produce a combination of fatty acids esters and an alcohol. When triglycerides are utilized, glycerol is produced. Transesterification reaction for biodiesel production is illustrated in Figure 1 below.

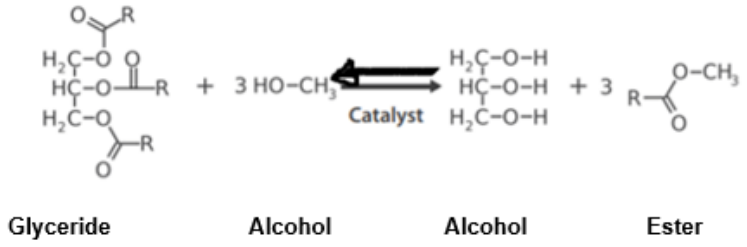

Figure 1. Transesterification reaction for biodiesel production.

When the reactants are mixed, a reversible process called transesterification occurs. You may apply a strong base or acid as a catalyst. In manufacturing, sodium, or potassium methanolate is often used on a large scale [22].

Both FAME and Neste Renewable Diesel are made from organic biomass however they are different products. Compared to FAME, Neste Renewable Diesel is mostly composed of waste and residues. Impurities are removed from raw materials throughout the manufacturing process, which is then hydrotreated at a high temperature. The end result is a colorless fuel of consistent quality with the same chemical composition as fossil diesel [36].

In comparison to fossil diesel, Neste MY Renewable Diesel, which is manufactured from 100% renewable raw materials, emits up to 90% fewer greenhouse gas (GHG) emissions across the fuel's entire life cycle. Neste MY Renewable Diesel, is also free of aromatics and other contaminants. As a result, maximum combustion efficiency for the fuel is achieved. As a result of its high cetane number (The cetane number, often known as the cetane rating, is a measurement of diesel fuel quality or performance) biodiesel is cleaner than traditional biodiesel (FAME). Therefore, Neste MY Renewable Diesel-powered fleets, tend to need less maintenance [36].

2.2 Radiocarbon

In the upper atmosphere the radioactive substance is formed naturally when cosmic radiation interacts with a stable isotope of nitrogen, producing a carbon atom with a mass of 14 and a proton, as shown in equation 1 where ${}^{14}_{7}N$= nitrogen, ${}^{1}_{0}n$= neutron, ${}^{14}_{6}C$= Radiocarbon and ${}^{1}_{1}p$= proton

$$ {}^{14}_{7}N + {}^{1}_{0}n = {}^{14}_{6}C + {}^{1}_{1}p \qquad (1) $$

Radiocarbon 14 (^{14}C) is a radioactive isotope of carbon that is unstable. Along with the stable isotopes ^{12}C and ^{13}C, it is the third naturally occurring carbon isotope. Radiocarbon 14 is a β -decaying isotope with a half-life of approximately 5730 years. In β -decay (beta decay) one of the protons or neutrons in a nucleus with too many protons or neutrons becomes another nucleus as it illustrated in Figure 2.

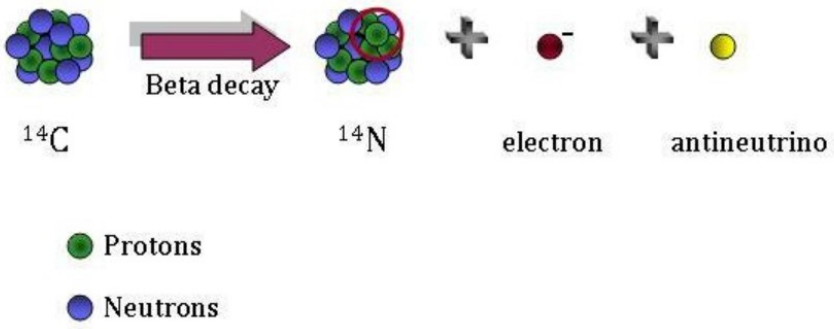

Figure 2. Radioactive decay of ^{14}C. One of the carbon atom's neutrons becomes a proton as a result of this reaction, which turns a ^{14}C atom into a ^{14}N atom. By adding one more proton to the atom, nitrogen is formed instead of carbon. During this process, an electron and an antineutrino, an elementary particle, are also generated [31].

Bioproportion can be determined due to the decomposition of radiocarbon. Additionally, radiocarbon is produced artificially as a result of human action. It is possible to determine bio proportion by determining the concentration of radiocarbon in a sample. When radiocarbon reacts with oxygen in the atmosphere (O_2), heavy carbon dioxide is produced. Air currents transport carbon dioxide containing radiocarbon throughout the atmosphere, all the way to the earth. Radiocarbon is transported to aquatic organisms when carbon dioxide binds with water. Most carbon is bound into plants by photosynthesis, where the plant gets CO_2 from air, which results in radiocarbon being transported to the plants. Radiocarbon is transported through the food chain and into a variety of organisms (including humans) [5].

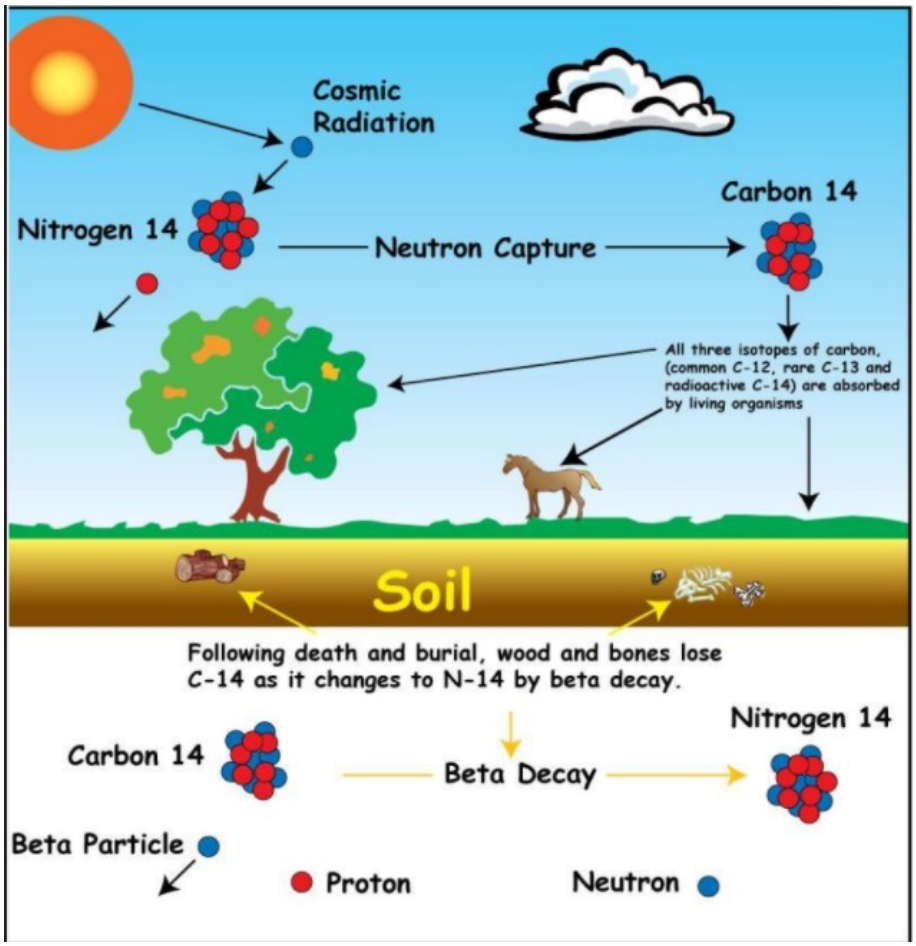

Figure 3. The emergence and decomposition of radiocarbon [37]. Radiocarbon (^{14}C) is formed from the upper atmosphere by cosmic radiation when secondary n neutron radiation from cosmic radiation collides with nitrogen ^{14}N. That is, when neutrons collide, the nitrogen 14 atom is converted to carbon 14 atom.

The radiocarbon content of organisms and plants is roughly equivalent to the radiocarbon content of the atmosphere. As the radiocarbon decays, one of its protons becomes a neutron, at the same time releasing antineutrino and an electron in accordance with formula 2.

$$^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + {}^{0}_{-1}e + \bar{\nu} \quad (1)$$

$^{14}_{6}C$= Radiocarbon

$^{14}_{7}N$= Nitrogen

$^{0}_{-1}e$= Electron

ṽ = Antineutrino

In 5730 years, half of the radioactive carbon in the carbonaceous material has been converted to nitrogen (Figure 4 below). Due to the fact that the quantity of ^{14} C in living organisms stays relatively constant regarding the quantity of cosmic radiation, the radiocarbon assay is suitable for determining bio proportion of renewable diesel. Because radiocarbon ^{14}C is present in living organisms throughout all times when they consume other matter or carbon dioxide, its decay is unaffected by its quantity. When living matter dies, the quantity of radiocarbon in the material decreases because it is no longer exchanged through photosynthesis or nutrition. Radiocarbon is very uncommon in comparison to other carbon isotopes [6].

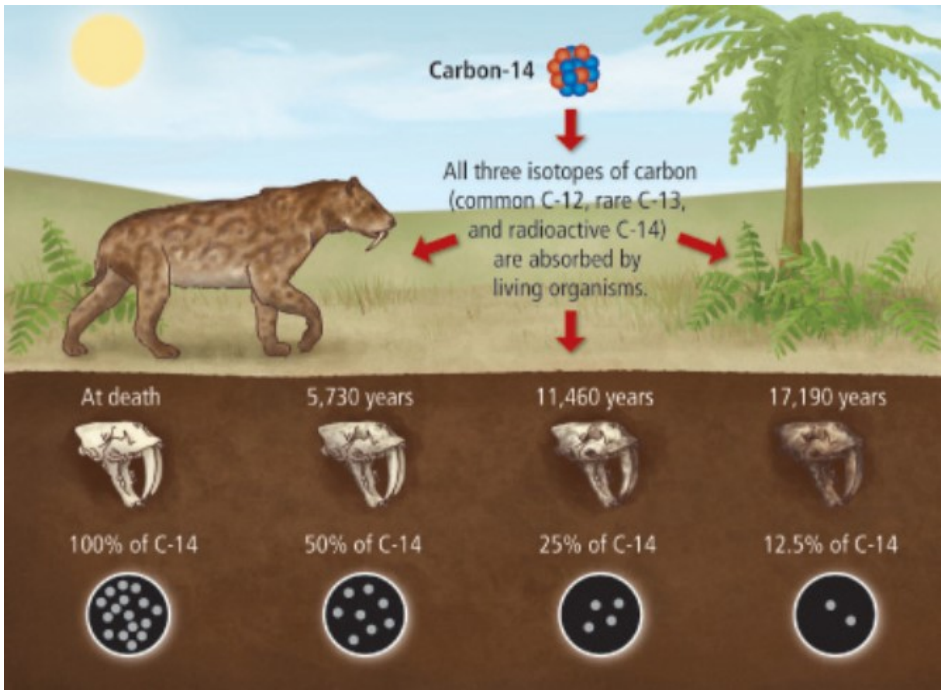

Figure 4. According to the half-life (5730 years), radiocarbon has already decayed in a fossil matter which has been in nature for a long time. In the new bio-based substance, the concentration of radiocarbon corresponds to the radiocarbon concentration of the atmosphere at that time [6].

Over the past 80 years, radiocarbon activity in our atmosphere has changed. The shift occurred as a result of the nuclear experiments performed between 1952 and 1963. Consequently, the atmospheric concentration of $^{14}CO_2$ increased by 90%. Radiocarbon reached its peak in the mid-1960s. In comparison to the period before the nuclear weapons testing, it had almost doubled. When nuclear testing ceased, the amount of radiocarbon started to decline once again. The amount of activated radiocarbon and its evolution in the atmosphere are shown in Figure 5 [7].

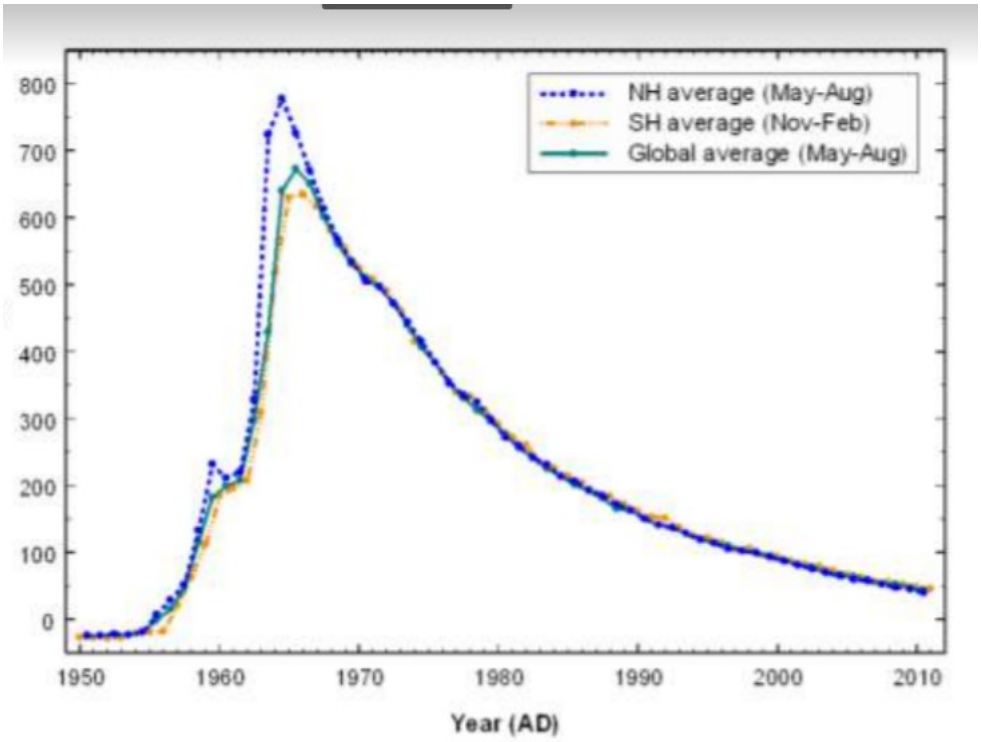

Figure 5. Radiocarbon measurement data in 1950 -
2010. Mean of atmospheric radiocarbon measurements in the Northern Hemisphere (NH) and Southern Hemisphere (SH) [7]. Y-axis shows radiocarbon activity level and X- axis show years before and after nuclear experiments was made.

Radiocarbon activity rose the most to a truly higher level in the northern hemisphere because most nuclear experiments were performed there. As shown in Figure 5, the activity level has gradually decreased to the same level as before the nuclear experiments in the 1960s. The level of carbon activity in the atmosphere should be taken into consideration in bio content measurements based on radiocarbon. The ASTM D6866-20 (Standard Test Methods for Determining the Biobased Content of Solid) standard determines annual levels of radiocarbon activity on nuclear tests from a

previous standard measurement. It has been determined according to ASTM D6866 that in the 1950s, before nuclear testing began, one gram of carbon in an ecosystem should have resulted in 13.56 dpm/g (dpm= disintegrations per minute per gram of barely calculated radioactive decays per minute). An annual coefficient of pMC (percent modern carbon) reference value was developed because after nuclear experiments 1 gram of carbon would give a larger number of flashes. The correction factor (REF) is based on the extra activity of radiocarbon in the atmosphere during the measurement.

A pMC reference value of 100 pMC in the assay means that the resulting gram of carbon should give 13.56 dpm. The effect of the coefficient on carbon activity may be calculated by dividing the 13.56 dpm value by one hundred and multiplying it by the yearly pMC reference value. Table 1 shows the activities of radiocarbon in the atmosphere for few years. Activity has been calculated with pMC (percent modern carbon) reference values and according to ASTM- D6866-20 [8, p.5–8].

Table 1. Radiocarbon activity level of a_{carbon} (atmospheric radiocarbon activity) in the atmosphere and correction factors (REFs) for six years. dpm/g refers to disintegrations per minute per gram and pMC refers to percent modern carbon.

Year	**a_{carbon} (dpm/g)**	**REF (pMC)**
2015	13,83	102,0
2016	13,76	101,5
2017	13,70	101,0
2018	13,63	100,5
2019	13,56	100,0
2020	13,56	100,0

The level of atmospheric radiocarbon activity (a_{carbon}) is obtained by dividing the pre-nuclear standard 13.56 dpm /g by one hundred and multiplying it by the correction factor for the measurement year. For example, the carbon activity level for 2020 is 13.56 dpm/g, which is obtained when using the year 2019 correction factor of 100.0 pMC. So (13.56 dpm / g ÷ 100) × 100 = 13.56 dpm / g [8, p.8]

2.3 Determination of biogenic content

There are many different methods that can be used to measure biogenic content and all of them are based on the measurement of radioactive carbon. Among these methods the most common methods are liquid scintillation counter and an accelerator mass spectrometer. Other methods are being developed as well, such as PIMS (Positive Ion Mass Spectrometry) and SCAR (Saturated Absorption Cavity Ring-Down Spectroscopy). The standard DIN 51637: 2015–04 describes the determination of biogenic content of renewable diesel by the direct liquid scintillation method. The method to be validated in this work is based on the standard DIN 51637: 2015–04.

Another technique for determining carbon 14 content is to utilize a gas proportional counter. Gas proportional counting is the name for this technique. Because beta particles are radiocarbon decay products, this technique converts the carbon sample to carbon dioxide gas before beginning the measurement in a gas proportional counter [20].

These method's principles are explained next. LSC and AMS methods are explained in further detail in section 2.3.1 and 2.3.2

2.3.1 Liquid scintillation counter (LSC)

The Liquid Scintillation Counter (LSC) is used to analyze low-energy radioisotopes, mainly alpha or beta-decaying isotopes. It is also used to measure X-rays or samples that emit Auger electrons. Auger electrons are emitted when an electron from a high-energy level fall into a vacancy in an inner shell. LSC is suitable for a wide variety of matrices that are liquid such as water or various fuels. The operation of the “Liquid Scintillation Counter” is based on electrons generated by radiation. Light can be generated in the discharge of the radiation excitation state and this light is detected by a

detector such as a photomultiplier tube. The light generated is converted into electric current by means of a detector as is shown in Figure 6 [9, p.4].

Liquid scintillation counting uses scintillation mixtures consisting of two different scintillation agents. The first scintillant emits excitation energy in the form of light, while the second scintillator adjusts the wavelength of the flashes of light to the desired range. The scintillant is always selected in accordance with the nuclide and sample matrix under study. Detection in LSC is based on the detection of radiocarbon decay event. The emitted beta particle causes solvent molecules to be excited, which then moves the excited state to scintillator molecules. Scintillator molecules release photons, which are then detected by photomultiplier tubes. Detection in LSC is summarized in Figure 6 [10].

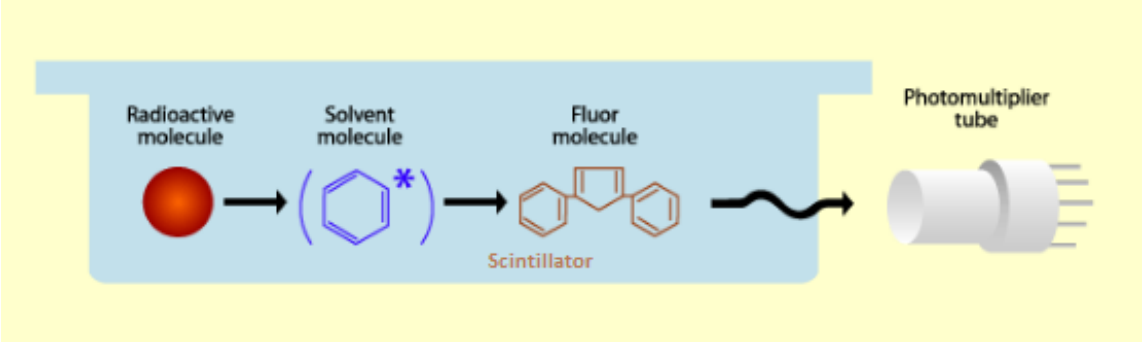

Figure 6. The liquid scintillation counter's operational principle. The energy released by radioactive decay excites the molecules in the sample solution and released radiation is transmitted to the scintillator and excites its electrons. The electrons' excitation state is discharged to the ground state, generating a light flash characteristic of the scintillator, and detected by the photomultiplier tube [10].

Sample processing for LSC is fast. Radiocarbon analysis is also the easiest radiocarbon analysis method in view of the fact that it is extremely straightforward and basic operation. The sample is dissolved in the scintillator in a ratio of 1: 1, after which the sample is ready for analysis. The photons of the scintillator beam to the photocathode of the photomultiplier tube by means of reflective surfaces. A photomultiplier tube is a

semipermeable photosensitive photocathode that emits electrons when light hits it. The electrons are accelerated by 10 to 14 electrodes (dynodes) connected in series. Electrons always multiply when they hit a new dynode that emits many new electrons. The number of electrons increases many times with each dynode, and eventually the number of electrons arriving at the detector is a million times higher than the initial situation [9, p.5]. Illustration of a scintillation counter is shown in Figure 7 below.

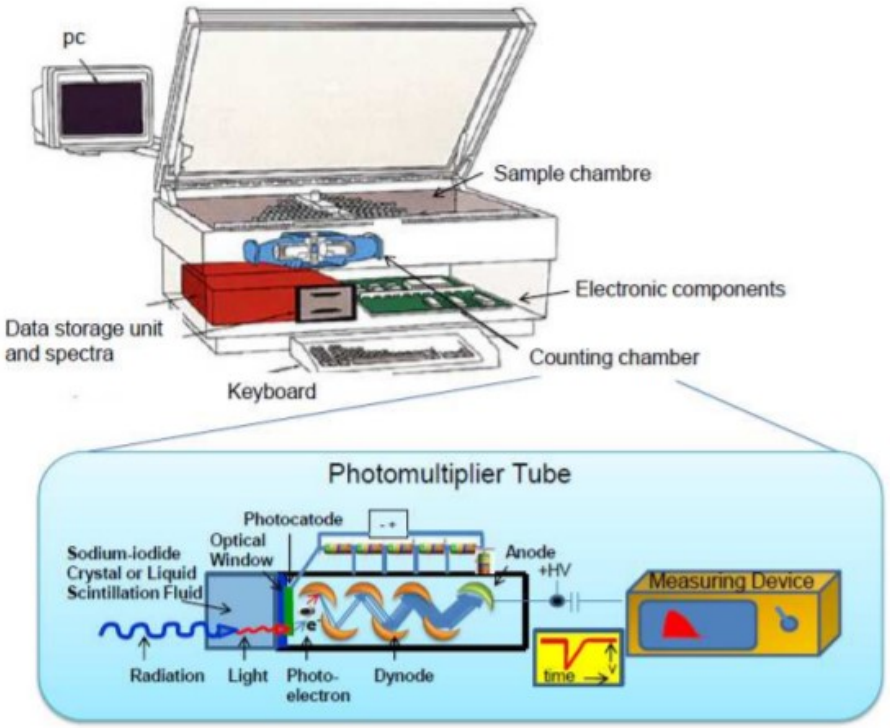

Figure 7. Ionizing radiation is detected using a scintillation counter [33].

When using a liquid scintillation counter, the effect of the measurement conditions on the calculation efficiency of the nuclide to be measured must be considered. This is affected by, among other things, attenuation, liquid scintillation solution, and liquid scintillation bottle material [11, p. 168]. Good computing efficiency is sought by following the conditions specified in DIN 51637:2015–04.

Quenching is a significant issue in liquid scintillation spectrometry. The irreversible absorption of decay energy or photons during the energy transfer from the decaying particle to the photocathode is referred to as quenching. Quenching affects the choice of

sample size, as the amount of sample is proportional to the amount of quench and to minimize quenching, the type and number of samples of the scintillation cocktail are selected in accordance with the recommendations of the equipment manufacturer [14].

There are three different types of quenches which are color quench, physical quench, and chemical quench. In the color quench the optical properties of a mixture of a sample and fluorescent agent are different from those of a fluorescent agent alone, allowing photons to be absorbed into the pigment in the sample, whereas in the physical quench, beta radiation is never removed without hitting the solvent and fluorescent molecule. In the third quench which is chemical quench, the solvent molecules or fluorescent molecules transmit their energy in a form other than becoming a photon [15].

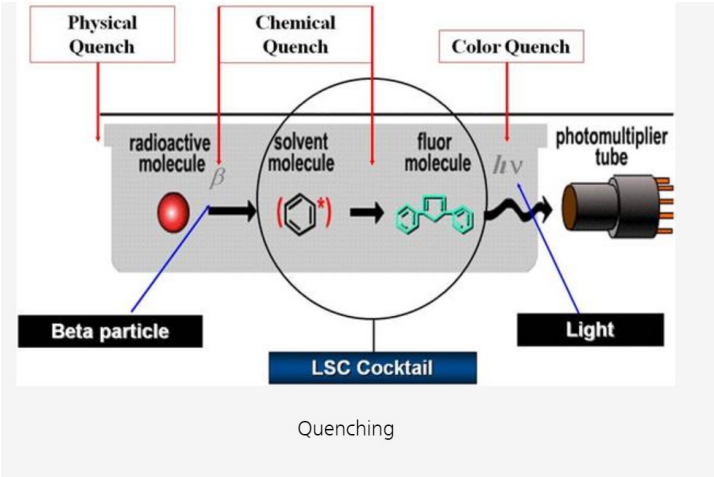

Figure 8: Quenching usually occurs when the energy emitted by the radioisotope is not caught entirely by the photomultiplier tube of the counting instrument. The signal reduction can occur at various stages of the energy transmission process. There are three types of quenches which are physical, chemical and color quench [16]

Quenching can be determined by many different methods, such as making a quench curve and an internal or external standard [16, p. 169–170]. The Perkin Elmer TriCarb 3180 TR / SL liquid scintillation counter has a quench curve, which means a set of standards in which the radiocarbon activity (dpm) of each sample is the same and the amount of attenuation varies. The damping curve aims to change the uncorrected counts per minute (cpm) into disintegrations(dpm). The measurement of the standards gives cpm values and, if the quench curve is successful, the dpm values for radiocarbon are also obtained. The efficiency (E) is calculated according to formula 3.

$$E = \frac{cpm \times 100}{dpm} \quad (2)$$

E= Efficiency

Cpm= Counts per minute

Dpm= Disintegrations per minute

When the attenuation curve has been determined and recorded, the activity of the samples to be measured in the future can be calculated using an external standard, flash and efficiency using formula 4.

$$dpm = \frac{cpm \times 100}{E} \quad (4)$$

cpm= Counts per minute

dpm= Disintegrations per minute

It should be considered that the sample is not completely carbon while calculating the bio content. Therefore, the carbon content of the sample is determined separately. By means of the radiocarbon activity of the sample, the annual atmospheric activity value, and the carbon content of the sample to be determined separately, the bio content of the samples as a percentage by mass can be calculated by formula 5.

$$m - \%_{bio} = \frac{\frac{dpm_n}{m_n} - \frac{dpm_0}{m_0}}{x_C \times a_C} \quad (5)$$

- dpm_n is the activity of the sample and its mass m_n.

- dpm_0 is the activity of the blank sample and m_0 is its mass
- X_c is the mass percentage of carbon in the sample divided by 100
- a_c is the annual atmospheric activity value of carbon

This formula (5) is from DIN 51637: 2015–04 standard where the bio content is calculated as a volume percentage [14, p. 12–13].

tSIE value can be determined in bio proportion determination. tSIE value indicates the color of the sample. The value of tSIE should be greater than 800 in an ideal sample, implying that the sample is clear and colorless.

The sample can be measured once the quench series and the energy window have been determined. Without forgetting that the number of flashes in a sample must be compared to a blank sample which is completely fossil to estimate its biogenic carbon. The number of degradation events must be related to the weight of the sample so in this case how many degradation events per minute are obtained per gram of sample. As it is mentioned in section 2.3.1 the sample is not completely carbon; thus, the carbon content of the sample must be considered. Another factor that must be considered is that the result is affected by the increase in radiation due to nuclear tests. Formula 5 (page 15) is used to calculate the result.

2.3.2 Accelerator mass spectrometry (AMS)

In general, AMS is a technique for measuring isotope ratios with high selectivity, sensitivity and precision. Accelerator mass spectrometry (AMS) separate a rare radioisotope from stable isotopes and molecular ions of the same mass using a variety of standard nuclear physics techniques. The ^{14}C ions are separated and counted as particles relative to ^{13}C or ^{12}C that are measured as an electrical current. When it comes to AMS allowing quantitative and specific measurement of isotopes the key steps are the production of negative ions from the sample to be analysed, the use of high energies which allow for the identification of ions with high selectivity and a molecular

disassociation step to convert the negatively charged molecular ions to positively charged nuclei [18].

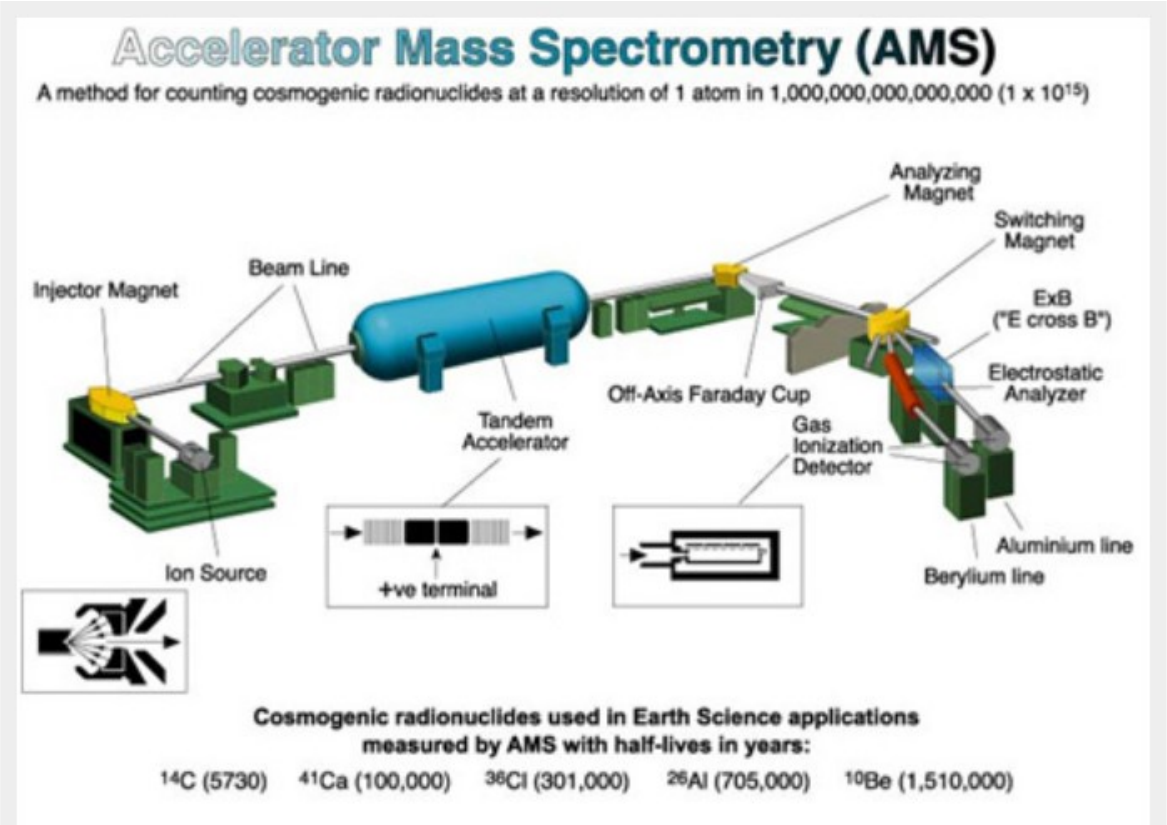

Figure 9. Radiocarbon dating by accelerator mass spectrometry is a two-step process. In the first part, the ions are accelerated to very high kinetic energies, and in the second step, the mass of the ions is measured [34].

An electrostatic double accelerator is used while measuring radiocarbon. The samples are reduced into solid carbon, compressed into a small plate, and placed in the ion source of an accelerator mass spectrometer. Ions are fired from the caesium gun into the sample plate, forming negatively ionized carbon atoms. The carbon atoms travel past the focusing devices and the injection magnet before reaching the double accelerator, where they are accelerated to the positive end of the accelerator by a voltage difference of up to several million volts. After acceleration, the other negatively charged atoms are unstable, so they do not travel to the detector. The carbon atoms continue to travel to

the “stripper”, losing electrons there and forming triple positively charged atoms ($14C^{3+}$). At this stage, all molecules are eliminated because they cannot be triple charged.

The positively charged carbon atoms are accelerated through other focusing devices where mass analysis takes place. In mass analysis, charged particles are subjected to a magnetic field that causes these particles to deviate from their path. Heavier particles traveling at the same speed deviate the least from their path and lighter ones the most. The detectors are set at different angles, allowing them to detect and count particles of a certain mass. Accelerator mass spectrometry (AMS) counts ^{14}C as individual nuclei and is independent of decay. About 10% of the ^{14}C in a sample is counted that means 1000-times more efficient than decay counting. The AMS technique is very sensitive, sensitivities approaching $^{14}C/C$ of around $2x10^{-15}$ or 10 attomoles of ^{14}C can be achieved in mg sized samples. Figure 9 and Figure 10 show the AMS system for the measurement of ^{14}C [18].

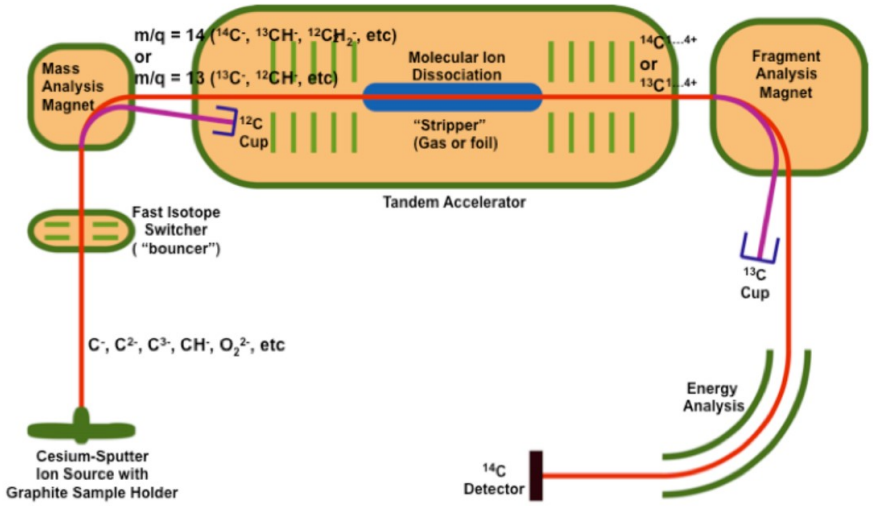

Figure 10: AMS system for the measurement of ^{14}C [18].

2.3.3 Comparison between LSC and AMS

The difference between Accelerator Mass Spectrometry (AMS) and liquid scintillation method is that the AMS does not calculate the decay events of radiocarbon, but the percentage of radiocarbon atoms in the sample. However, each method has their advantages and disadvantages which are mentioned in table 2 below.

Table 2. Advantages and disadvantages between AMS and LSC [19]

Liquid Scintillation counting (LSC)	**Accelerator mass spectrometry (AMS)**
Advantages – Lower cost both for the instrument and per analysis – Good instrument availability, suitable for normal laboratories. – Lower risk for contamination of the sample – Various sample preparation methods available – Immediate analysis with direct measurement can be used for liquid sample – Higher amount of the sample enables better representativeness **Disadvantages** – For some sample preparation protocols, additional devices needed – Need for a low-level counter to overcome background issues – Matrix dependency – Inability to measure heavily coloured samples – Inability to measure gases or solids	**Advantages** – Low amount of sample needed – Very high sensitivity – Precise analysis – Ability to measure nearly any type of sample.Matrix independency **Disadvantages** – Need for a graphite conversion device – High cost for the instrument – Complex technology, need for specific laboratory and expertise – Higher risk for contamination of the sample – Lower amount of the sample is associated with poor representativeness, and higher number of replicates needed.

3 Validation parameters used in method development

The purpose of validation is to establish that an analytical method is suitable for its intended use. Validation can also be defined as the process through which laboratory studies establish that the method's performance characteristics match the criteria for the intended analytical applications. The liquid scintillation counter method's linearity and accuracy were evaluated throughout the validation process

3.1 Linearity

The capacity of an analytical technique to produce an acceptable linear correlation between results and the concentration of a test substance in a sample across a range is referred to as linearity. It is usually suggested that the linearity can be determined using at least five traceably prepared products of various concentrations, as well as a sample (in addition to the blank) whose concentration of the chemical to be tested covers the whole measurement range. Several repeats are done at each concentration if possible. Using the least squares technique, the results are utilized to create a regression line. The linear range of the technique may be visually evaluated using this graph. [23, p.28-29]. A common way to measure linearity is to assign to the graph the square of the correlation coefficient of the linear fit, R^2. Excel is a good tool for this. R^2 0.995 or R^2 0.999 are two commonly accepted limit values [24, p.19].

It is also a good idea to use a regression line to look at residuals when evaluating linearity. The discrepancies between the measured and calculated y-values from the regression line, which may be calculated using formula 6, are known as residuals (ε).

$$\varepsilon = y_i - v_i \tag{6}$$

- y_i = describes the measured y-values
- v_i = describes the y-values calculated from the regression line.

If the measurement range is linear, residuals are equally distributed on both sides of the zero. If the residuals form a clearly discernible curve, it is possible to decrease the measurement range or fit the residuals using, for example, the equation of a straight line [25, p.14].

3.2 Accuracy

3.2.1 Precision

Precision is the degree of agreement between individual test results gathered when the technique is repeated on numerous samples from a homogenous sample. A test method's precision is often represented as the standard deviation or relative standard deviation of a set of measurements. It is a measure of the analytical method's reproducibility or repeatability under typical operating conditions. The precision is expressed in terms of RSD %. Parameters like standard deviation (SD) and relative standard deviation RSD (coefficient of variation) should be reported.

The standard deviation and relative standard deviation of multiple measurements may be used to determine the precision. A random error impacts the number of the result at random and may be caused by a variety of factors, including changes in conditions or negligent actions. the standard deviation (s) can be calculated by using the formula 7 where xi is a single measurement value and $\bar{x}$ is the average of the measurements. N means the number of measurement repetitions.

$$s = \sqrt{\frac{\sum_i^n (x_i - \bar{x})}{n-1}} \quad (7)$$

The relative standard deviation (RSD) can be calculated from the standard deviation (s) and the mean ($\overline{x}$) using the formula 8. Performing measurements as quickly as possible may also assist in the maintenance of comparable conditions.

$$RSD = \frac{s}{\bar{x}} \times 100\ \%. \tag{8}$$

Precision may be thought of on three levels and these levels are Repeatability, intermediate precision, and reproducibility. The term "repeatability" refers to the precision achieved when the same operating conditions are repeated over a short period of time. A minimum of nine determinations covering the given range should be used to determine repeatability. Intermediate precision reflects within-laboratories variations, such as different days, different analyzers, and different equipment. Reproducibility refers to the consistency of results between laboratories. It is evaluated via an interlaboratory study [25, p.19].

3.2.2 Trueness

Trueness is the extent to which the found value agrees with the conventional true value or an accepted reference value. Accuracy should be proven throughout the analytical procedure's defined range. Trueness may be determined by comparing the average laboratory results to the average of laboratory results measured using a known method or a known reference material. The most true results are achieved when the reference material is identical in concentration and composition to the real samples. Trueness (E) may be calculated using the formula 9.

$$E = \frac{|\bar{x} - \mu|}{\mu} \times 100, \tag{9}$$

- $\bar{x}$ = the average of laboratory measurements

- μ= represents the known value or average of the reference material or method of analysis [26].

As it is explained in previous sections precision refers to how closely measured values are to one another. Trueness is the distance between a measure value and its actual value. The difference between trueness and precision, as well as their impact on measurement accuracy, are shown in Figure 11 [28].

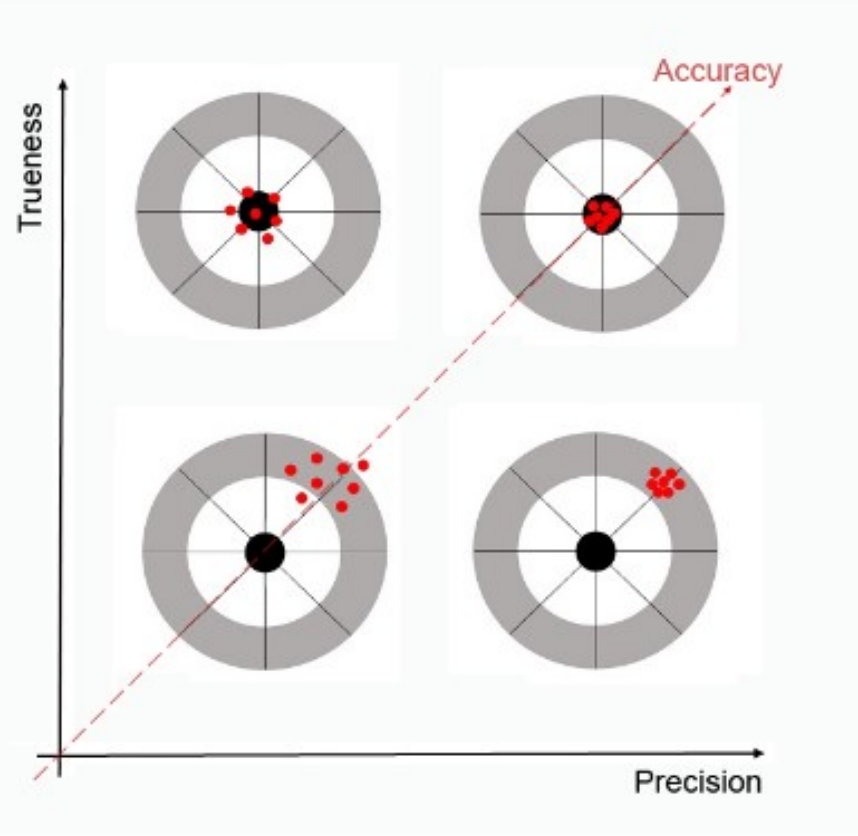

Figure 11. Precision vs trueness. trueness improves as the y-axis moves upward, while precision increases as the x-axis moves to the right.

As is shown in figure 11 accuracy improves when trueness and precision increase. When only the trueness is good, but precision is insufficient the measurement results will hit the target, but they will spread over a wide area which means the average of the results is close to the correct value and good, but the precision of the result is insufficient. If, on the other hand, precision is high, but trueness is low, the result will fall short of the goal but will be near it.

3.3 Limit of detection & Limit of quantification

The limit of quantitation (LOQ) of an analytical method is the smallest quantity of analyte in a sample that can be quantified with reasonable precision and trueness. Numerous methods of establishing the quantitation limit are possible, depending on the nature of the process (non-instrumental or instrumental).

The limit of detection (LOD) is the smallest quantity of analyte that can be detected but not necessarily quantified in a sample under the specified experimental circumstances. The detection limit may be determined in a variety of ways, depending on whether the technique is non-instrumental or instrumental. Other methods may be acceptable for both limit of detection and limit of quantitation in addition to those mentioned below.

3.3.1 LOD and LOQ Based on standard deviation of blank

The measurement of the analytical background response is determined by analysing enough blank samples and determining their standard deviation. LOD is calculated according to the formula 10 where $\bar{x}_0$ is the mean of the blank samples and s_0 is the standard deviation. As it is shown in formula 11 the limit of quantitation (LOQ) is determined in the same way as the detection limit. The only difference is that the standard deviation of the sample has a higher coefficient. While calculating the LOQ, it must be considered that the precision and accuracy remain within the desired limits [29]

$$LOD = \bar{x}_0 + 3s_0 \quad (10)$$

$$LOQ = \bar{x}_0 + 10s_0 \quad (11)$$

3.3.2 LOD and LOQ Based on Signal-to-Noise

This technique is applicable exclusively to analytical processes that show baseline noise. The signal-to-noise ratio is determined by comparing measured signals from samples with known low analyte concentrations to those from blank samples and determining the lowest concentration at which the analyte can be reliably detected.

Only the limit of determination can be estimated at low concentrations. The variance and standard deviation considered in the limit of determination are unacceptably large, since individual sample results are expected to vary significantly with very low sample concentrations. The methods are meant to assist in the accuracy of the limit of quantification determined from blanks and the regression line; they cannot be used to estimate the limit of quantification on their own.

Generally, a signal-to-noise ratio of 3 or 2:1 is considered acceptable for determining the limit of detection (LOD). when it comes to the limit of quantitation, a typical signal-to-noise ratio for its determination is 10:1 [30, p.1].

4 Execution of method development

4.1 Equipment and reagents used in method development

The following equipment and reagents (Figure 12) were used for developing the method for the determination of the biogenic content of carbon using Liquid Scintillation Counter (LSC):

- Liquid scintillation counter, Perkin Elmer, Tri-Carb 3180 TR/SL (Figure 13)
- Analytical balance, Mettler Toledo XSE205, Dual Range, max. 81/220 g.
- Liquid scintillation cocktail, Ultima GoldTM F, Perkin Elmer.

- Fossil diesel, Neste Oyj
- Neste MY renewable diesel™ (NRD), Neste Oyj
- FAME (fatty acid methyl ester)
- GTL

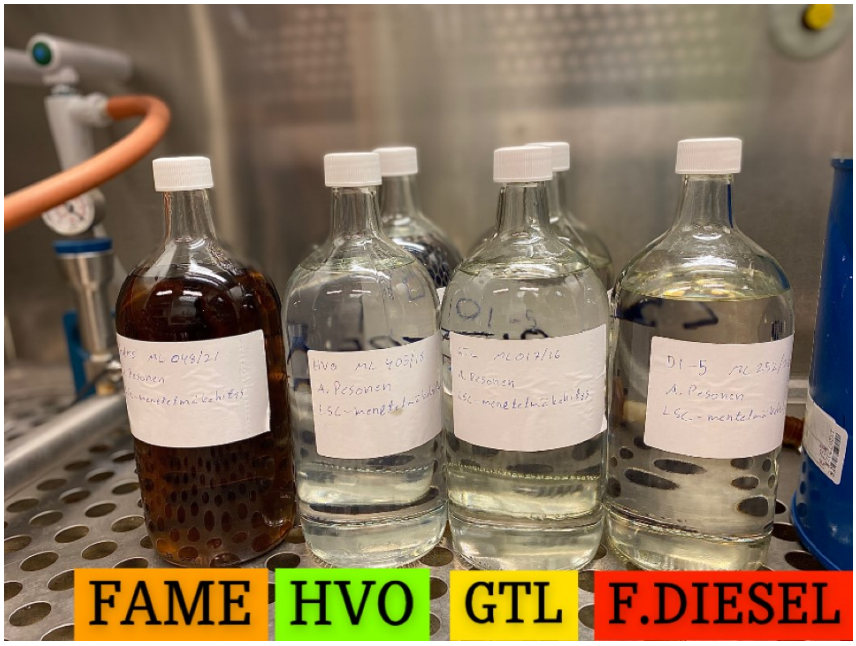

Figure 12. Reagents used in method development

In this method development a Perkin Elmer TriCarb 3180 TR / SL liquid scintillation counter was used (Figure 14). This scintillation counter has a few physical characteristics that it uses to ensure the quality of detection and effective attenuation of background radiation. The device has a lead shield to prevent background radiation from entering the device. The device also has two photomultiplier tubes, and it counts only two flashes that arrive at the detector at the same time as a signal. This is because the β-particles often excite several fluorescent molecules, which causes many photons to be generated within a short time window during the decay event. Therefore, only the signal entering the second photomultiplier tube is likely caused by background radiation [12]. The Perkin Elmer TriCarb 3180 TR / SL liquid scintillation counter also has a bismuth germanium oxide (BGO) sheath around the detector, which has a longer fluorescence life than the fluorescent molecules in the liquid scintillation cocktail. The tuning of the BGO allows the scintillation counter to detect the difference between external radiation and radiation caused by the sample in detection [13].

4.2 Preparation of standards and sample

Standard samples were prepared for the measurements. A changing diesel sample matrix was created, and 11 standard samples were prepared using it (table 3). A blend of fossil fuel, NRD, and FAME was used in these samples. Another 11 fossil samples were prepared using a changing fossil matrix (CFM) (table 4), including NRD, fossil diesel, and GTL in the blend. Standards samples were measured in 60ml dark glass flasks. After preparing the standard samples, they were placed in the laboratory refrigerator to prevent luminescence from affecting the results.

Table 3. Changing biobased matrix (CBM)

Sample name	**Fossil diesel v-%**	**NRD v-%**	**FAME v-%**
CBM-1	50 %	50 %	0 %
CBM-2	50 %	45 %	5 %
CBM-3	50 %	40 %	10 %
CBM-4	50 %	35 %	15 %
CBM-5	50 %	30 %	20 %
CBM-6	50 %	25 %	25 %
CBM-7	50 %	20 %	30 %
CBM-8	50 %	15 %	35 %
CBM-9	50 %	10 %	40 %
CBM-10	50 %	5 %	45 %
CBM-11	50 %	0 %	50 %

Table 4. Changing fossil matrix (CFM)

Sample name	Fossil diesel v-%	NRD v-%	GTL v-%
CFM-1	50 %	50 %	0 %
CFM-2	45 %	50 %	5 %

CFM-3	40 %	50 %	10 %
CFM-4	35 %	50 %	15 %
CFM-5	30 %	50 %	20 %
CFM-6	25 %	50 %	25 %
CFM-7	20 %	50 %	30 %
CFM-8	15 %	50 %	35 %
CFM-9	10 %	50 %	40 %
CFM-10	5 %	50 %	45 %
CFM-11	0 %	50 %	50 %

CBM and CFM samples were prepared for a liquid scintillation counter measurement in sample vials made of polypropylene to reduce the amount of electricity. In a fume hood (Figure 13), an eight-gram sample was weighed to the closest 0.1 mg using Sartorius Mettler Toledo XSE205 scale.

Figure 13. Samples were prepared in a fume hood in the quality control laboratory in Porvoo.

Following the addition of the sample to the sample vial, 10 ml of Ultima GoldTM F liquid scintillation cocktail was added, with a sample-to-cocktail ratio of 1: 1 since 8 grams of sample equals approximately 10 ml. The used scintillation cocktail was manufactured by the device manufacturer. Since even a little contamination of the vial's exterior surface might have contaminated the device's detector, the sample vial was handled with care and clean gloves.

4.3 Measurement of samples

The carriage was placed into the device as it shown in Figure 14, and the device's identification was displayed so that the sample data could be recorded to the computer.

Figure 14. Interior of the liquid scintillation counter, where the samples are put. The samples were placed in a liquid scintillation counter in a plastic sample carriage.

The aim was to measure all changing biobased sample matrix (CBM) and changing fossil sample matrix (CFM) samples as many times as possible to increase the amount of data available for result processing. The CBM samples were the first to be measured. The result was observed immediately after the first round of CBM sample measurements and realized that LSC was unable to measure the CBM samples. According to the changing biobased matrix (CBM) (table 3, p.27) these samples include fatty acid methyl ester (FAME). On the basis of the results, heavy luminescence and extremely low tSIE values were observed with CBM samples, particularly those with a greater proportion of FAME (table 5).

Table 5. CBM high FAME content sample's tSIE values.

Sample name	FAME v-%	tSIE
CBM-1	0 %	816,77
CBM-2	5 %	220,35
CBM-3	10 %	220,35
CBM-4	15 %	84,64
CBM-5	20 %	67,30
CBM-6	25 %	94,76
CBM-7	30 %	46,51
CBM-8	35 %	38,95
CBM-9	40 %	37,84
CBM-10	45 %	32,92
CBM-11	50 %	32,98

After calculating the biogenic carbon mass percentage, it seemed that the more FAME there was in the sample, the lower the biogenic carbon mass percentage value was. It was suspected that the results obtained were due to heavy color quench since it is known that fatty acid methyl ester contains color (color of sample can be seen in Figure 12, p.26). The results of the first round of changing biobased matrix (CBM) samples are shown in table 6.

Table 6. The results of the first round of changing biobased matrix (CBM) samples.

Sample name	dpm	cpm	biogenic carbon mass %
CBM-1	49,49	39,85	49,46
CBM-2	47,08	33,33	46,84
CBM-3	44,38	31,06	43,90
CBM-4	43,38	17,61	42,81
CBM-5	34,66	12,13	33,33
CBM-6	25,02	8,90	22,79
CBM-7	22,08	7,08	19,60
CBM-8	20,03	5,71	17,37
CBM-9	19,17	4,89	16,45
CBM-10	18,44	4,41	15,65
CBM-11	16,8	4,02	13,86

It was not possible to continue measuring CBM- samples with higher FAME concentrations; therefore, 5 additional CBM samples (CBM-12 to CBM 16) were blended with lower FAME percentage to the matrix, and these samples were measured five times. Changing biobased matrix (CBM) with lower content of fatty acid methyl ester is shown in table 7.

Table 7. Changing biobased matrix (CBM) with lower content of fatty acid methyl ester

Sample name	**Fossil diesel v-%**	**NRD v-%**	**FAME v-%**
CBM-12	50 %	46 %	4 %
CBM-13	50 %	47 %	3 %
CBM-14	50 %	48 %	2 %
CBM-15	50 %	49 %	1 %
CBM-16	50 %	49.50 %	0.50 %

By filtering the samples, the color of CBM- samples was decreased. The samples with the higher FAME content (CBM-2 to CBM-11) were measured twice. The samples were filtered once for the first measurement and twice for the second measurement. The samples with lower fatty acid methyl ester concentration (CBM-12 to CBM-16) were filtered as well. These samples were filtered once before being measured in two rounds. For the changing fossil matrix (CFM) samples the expected result could be seen after the first round of measurement; therefore, these samples were measured three times.

In addition, a total of 15 samples were also sent to the external AMS laboratory of University of Helsinki for the reference measurements. Samples that were sent were Fossil diesel, GTL, HVO, FAME, CBM-2, CBM-4, CBM-8, CBM-10, CFM-2, CFM-4, CFM-8, CFM-10. Sample of low content of FAME (CBM-12 to CBM-16) were sent as well. All the samples were sent in tightly closed glass sample bottles.

5 Results and results analysis

5.1 CBM series non-filtered samples

5.1.1 Linearity

The linearity of a measured CBM samples with high content of FAME's regression line and its residuals were analyzed, and the regression line was created by using eleven measurement points from samples CBM-1 to CBM-11. These samples were high FAME content and non-filtered samples (Table 3, p.27).

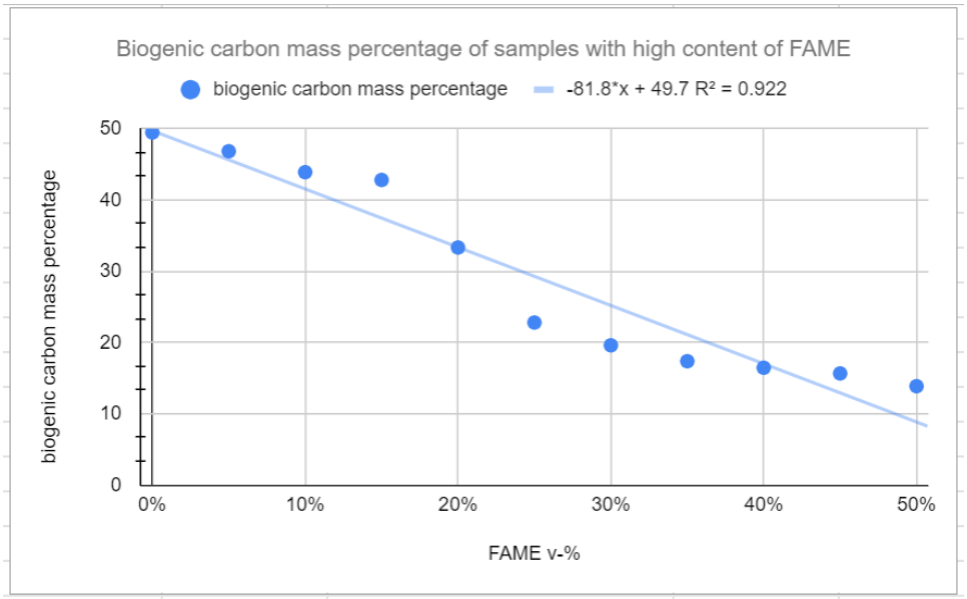

Figure 15. Biogenic carbon mass percentage of samples with high content of FAME (v-%)

The regression line in Figure 15 shows that the correlation between biogenic carbon mass percentage and FAME v % seems to be non-linear, with a correlation value of 0.922. Based on the graph, a residual diagram was also created (Figure 16). Formula 6 (p. 20) was used to determine residuals.

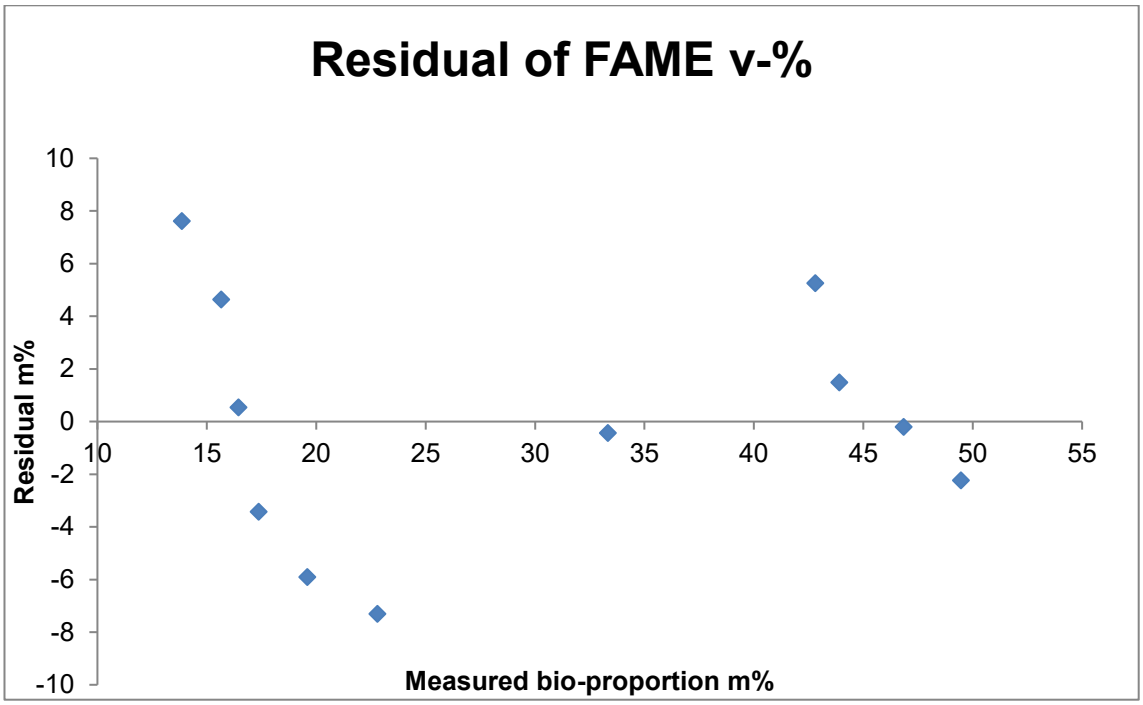

Figure 16. Residual of FAME-v%. Residuals were calculated using a regression line equation.

The biogenic carbon mass percentage of the samples measured at all concentrations was in some way distributed on both sides of zero; as seen on the graph. However, residuals appear to rise slightly from a higher to a lower concentration. Meaning that the linear model is good fit for relatively small x- values (CBM samples with low FAME content) but is not a good predictor of larger x- values (CBM samples with high FAME content). When the regression line and its residual are examined, it can be seen that the more FAME is present in the sample, the more the measurement is disrupted which means the less FAME there is in the sample, the less liquid scintillation counter detects flashes.

5.1.2 Precision and trueness

The trueness and precision of systematic and random error were measured. To evaluate trueness, the averages of the results of CBM samples (table 8) measured from liquid scintillation counter and correct values from AMS laboratory were calculated according to formula 9 (p.22). Deviations from the true value (bias) and percentage deviations were calculated from the averages. Table 8 summarizes the averages of the biogenic content measured from the liquid scintillation counter and the AMS-laboratory.

Table 8. Relative deviations between LSC measurements and reference measurements (AMS).

Sample name	**FAME V%**	**Measured in LSC**	**True value (Measured in AMS)**	**Bias (deviation from the true value)**	**Relative deviation (%)**
FAME	100	4.85	106.56	-101.71	95.45
CBM-2	5	46.84	49.06	-0.56	4.53
CBM-4	15	42.81	50.98	-8.17	16.03
CBM-8	35	17.37	47.91	-30.54	63.75
CBM-10	45	15.65	47.73	-32.08	67.21
CBM-12	4	48.03	49.66	-1.63	3.29
CBM-13	3	47.76	50.91	-3.15	6.18

CBM-14	2	48.02	48.38	-0.36	0.75
CBM-15	1	47.97	49.13	-1.16	2.36

CBM-10 has the highest relative deviation. When compared to other samples, this sample has the highest FAME content. Relative deviation decreases especially when going to lower concentrations of FAME in samples. For FAME sample and for the samples with higher content of FAME, the difference may be caused by the color quench that takes place during the measurement of the samples in liquid scintillation counter. Due to this, the method's accuracy worsens at higher concentrations, we can already observe that after the sample CBM-2 with 5 % FAME, the relative deviation changes significantly.

However, for samples with lower content of FAME, sample CBM-13 with 3 % of fatty acid methyl ester has a slightly higher relative deviation (6.18) than the sample CBM-2 with 5 % (4.53) of FAME; the same occurs between CBM-15 (1 % of FAME with 2.36 of relative deviation) and CBM-14 (2 % of FAME with 0.75 of relative deviation). It is possible that this is because the less fatty acid methyl ester in the sample (less than 1 %), the fewer flashes liquid scintillation detects, contributing to an increase in the relative deviation. In this instance, the flash that is not noticed by LSC has a greater effect on the results than when there are more lights in samples with more than 1 % of FAME but less than 5 % of FAME. This implies that when FAME concentration in a sample is more than 5 % and less than 1 %, accuracy worsens. Another explanation may be that the reference samples measured in accelerator mass spectrometry (AMS) were measured only once meaning that there was not sufficient data. The comparison between the results of the samples from LSC and AMS is shown in Figure 17.

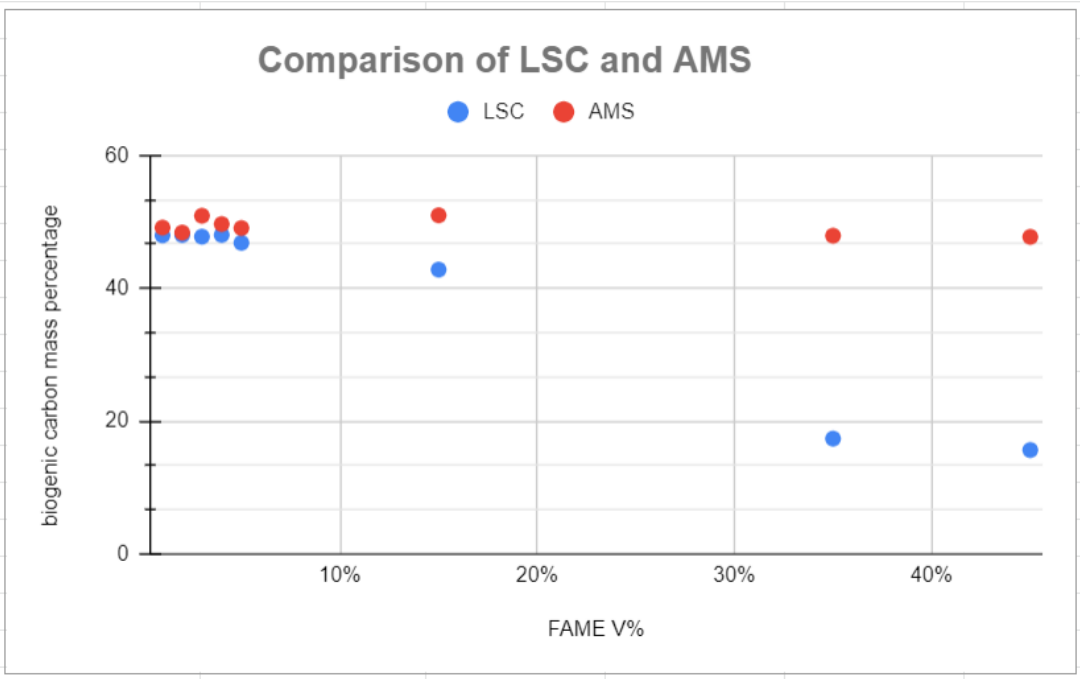

Figure 17. Comparison between CBM samples measured in liquid scintillation counter (LSC) and accelerator mass spectrometry (AMS)

Because the samples with higher content of FAME (CBM-1 to CBM-11) were measured only once, the standard deviation and relative standard deviation (RSD) of biogenic carbon mass percentage of the measurement repetitions of lower content of FAME samples (CBM-12 to CBM-16) were used to examine the precision. Standard deviation of samples shown in table 9 were calculated according to formula 8 (p.22).

Table 9. Averages, standard deviations, and relative standard deviations of low FAME concentration samples BM-12 to CBM-16.

Sample name	FAME%	Average	Standard deviation	RSD
CBM-12	4	48.03	1.33	2.77
CBM-13	3	47.76	0.73	1.53
CBM-14	2	48.02	0.66	1.37
CBM-15	1	47.97	0.26	0.54
CBM-16	0.5	48.28	0.62	1.29

The relative standard deviation of the measurements is much higher at the start of the measuring range and decreases as concentrations increase but increases from the samples with the lowest concentration of FAME to the highest. It is at its best between CBM-13 and CBM-14. It can also be observed that between sample CBM-15 and CBM-16 that relative standard deviation increases when FAME concentration in the sample falls below 1 %, implying that precision improves from samples with 2% FAME content to samples with higher FAME content. That is to say the lower FAME content in the sample is, the more the device's own uncertainty affects the result as a relative number.

Results for low FAME content sample series given in table 9 are portrayed in Figure 18. The results are constantly around 50 %, and because it is known that all the samples have 50 % bio-content, we can say with absolute certainty that LSC has the ability to measure samples with FAME concentrations of at least less than 5 %.

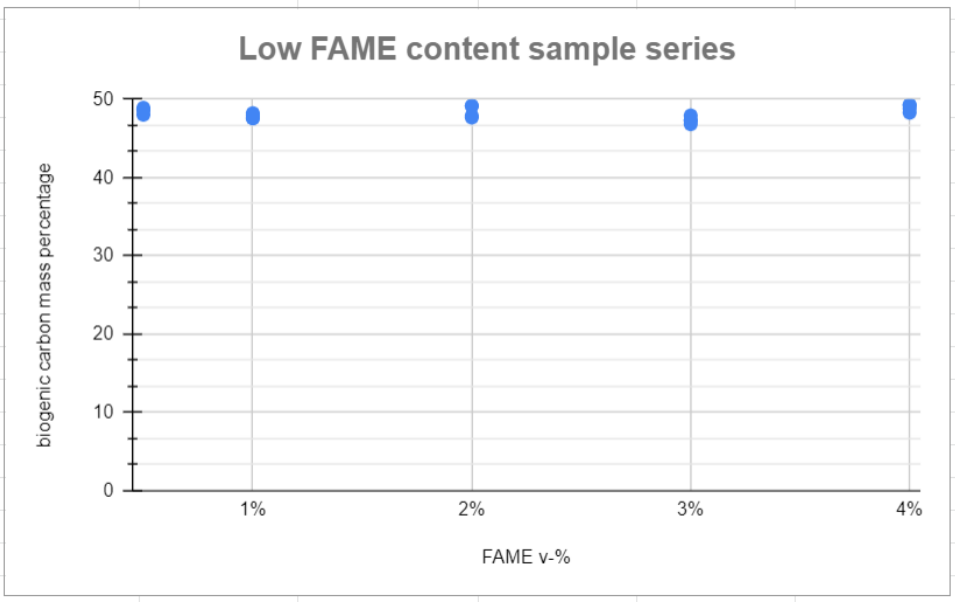

Figure 18. Low FAME content sample series.

Figure 19 shows the difference between samples with high and low FAME content, showing that samples with high FAME concentrations had lower biogenic carbon mass percentage than samples with low FAME concentrations, the more FAME in the sample, the lower the value of biogenic carbon mass percentage. This occurs because FAME samples include color, which produces color quench during LSC measurements.

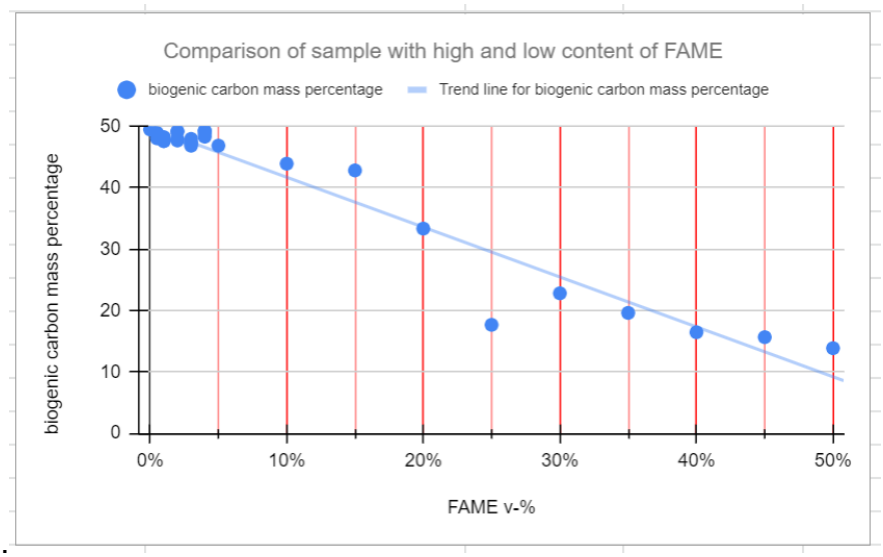

Figure 19. Comparison of sample with high and low content of FAME measured in LSC.

5.2 CBM- Filtered samples

5.2.1 Trueness

Trueness was also used to evaluate the results of filtered CBM samples. Only samples that were sent to AMS laboratory were used for trueness evaluation. The averages of the results of filtered CBM samples (table 10, p.39) measured from liquid scintillation counter and AMS laboratory were calculated according to formula 9 (p.22). Deviations from the true value (bias) and percentage deviations were calculated from the averages. Table 10 summarizes the averages of the biogenic content measured in liquid scintillation counter and the AMS-laboratory.

Table 10. Relative deviations between LSC measurements for filtered samples and reference measurements (AMS).

Sample name	FAME v%	Measured in LSC (Filtered once)	True value (Measured in AMS)	deviation from the true value (Bias)	Relative deviation (%)
CBM-2	5 %	46.94	49.06	-2.12	4.32
CBM-4	15 %	44.79	50.98	-6.19	12.14
CBM-8	35 %	39.52	47.91	-8.39	17.51
CBM-10	45 %	25.79	47.73	-21.94	45.97
CBM-12	4 %	47.21	49.66	-2.45	4.94
CBM-13	3 %	48.22	50.91	-2.69	5.28
CBM-14	2 %	48.14	48.38	-0.24	0.50
CBM-15	1 %	48.14	49.13	-0.99	2.01

Table 10 shows that relative deviations for filtered samples are significantly lower than for non-filtered samples. Because the color quench is decreased during measurement by filtering the color from the sample, the relative deviation decreases substantially when the color is filtered from the samples before measurement in LSC. Relative deviation decreases from samples with high FAME content to those with low FAME concentration , which means that as the concentration of FAME in CBM samples decreases, accuracy improves. Additionally, this simply means when color is filtered from samples containing FAME, accuracy improves. As it is noticed with non-filtered samples CBM-2 has a lower relative deviation than CBM-13, the same occurs between CBM-14 and CBM-15 as well. Differences between these samples is due to the same cause as for non-filtered samples explained in section 5.1.2.

The difference between high concentration of FAME filtered samples and non-filtered samples with high concentration is illustrated in Figure 20 where it is clearly noticeable that by filtering color from CBM-samples biogenic carbon mass percentage results improves. The significant difference in results is seen in samples with high FAME content, especially between samples with 20 percent to 35 percent of fatty acid methyl ester.

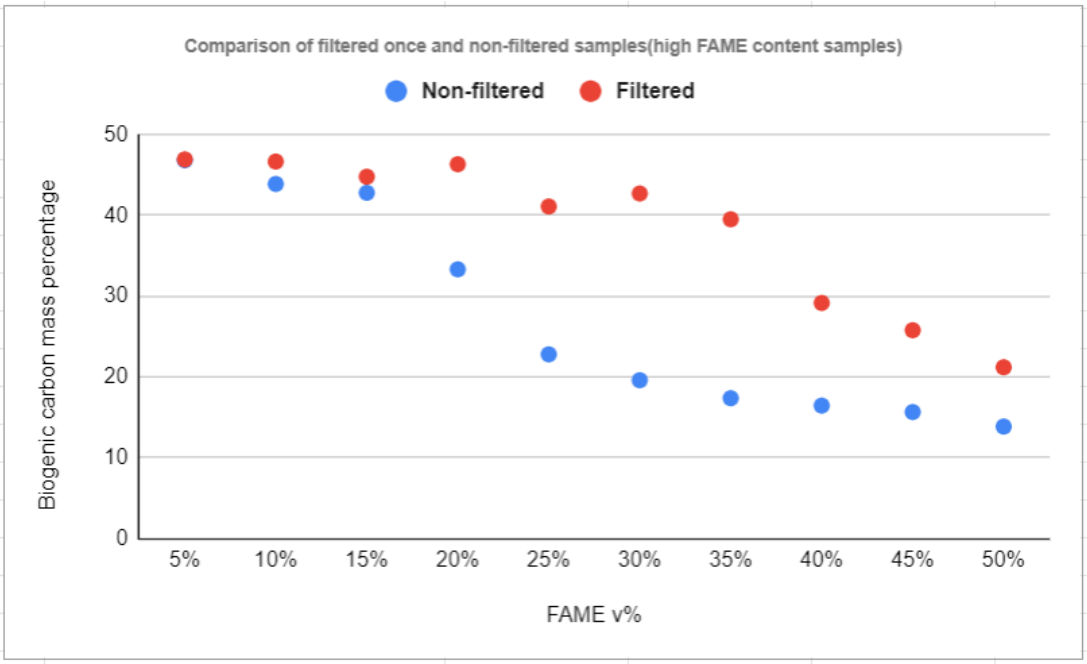

Figure 20. Comparison of high concentration of FAME filtered samples and non-filtered samples.

The difference between samples with high concentration of FAME that are filtered twice and non-filtered samples with high concentration is illustrated in figure 21. Biogenic carbon mass percentage values improve more than for samples that were simply filtered once (figure 20), and the values of biogenic carbon mass percentage are more constant than for samples filtered twice. Samples with high FAME concentration show a substantial variation in result as well.

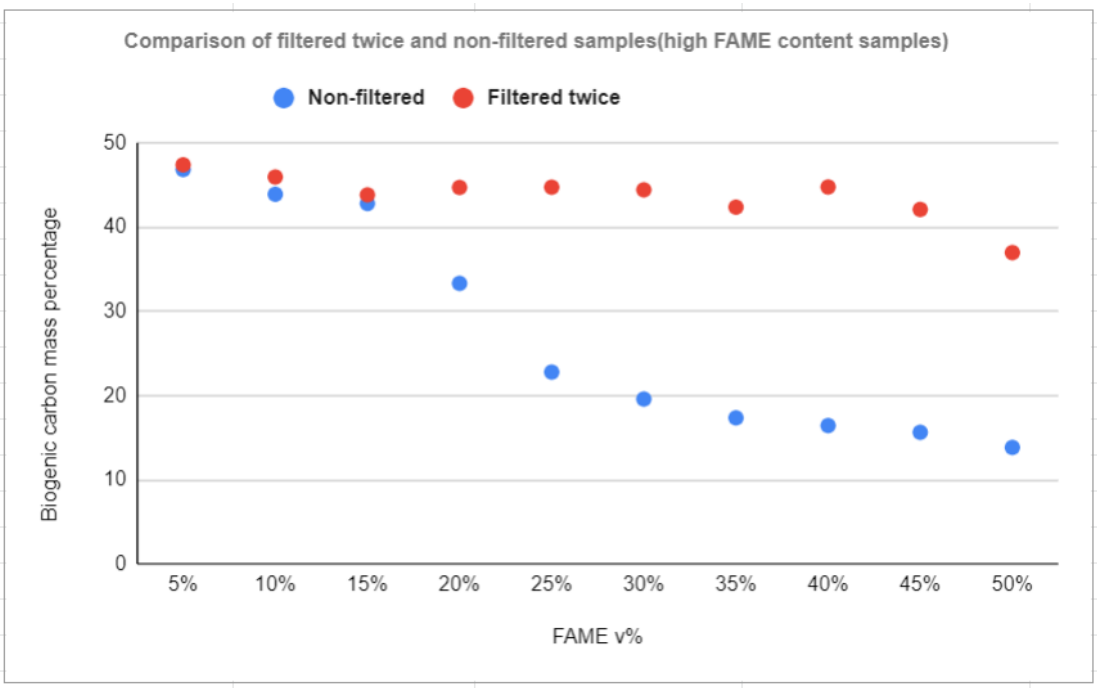

Figure 21. Comparison of samples with high concentration of FAME that are filtered twice and non-filtered.

Figure 22 (p. 42) illustrate the difference between CBM samples with high FAME content that are not filtered, filtered once, and filtered twice

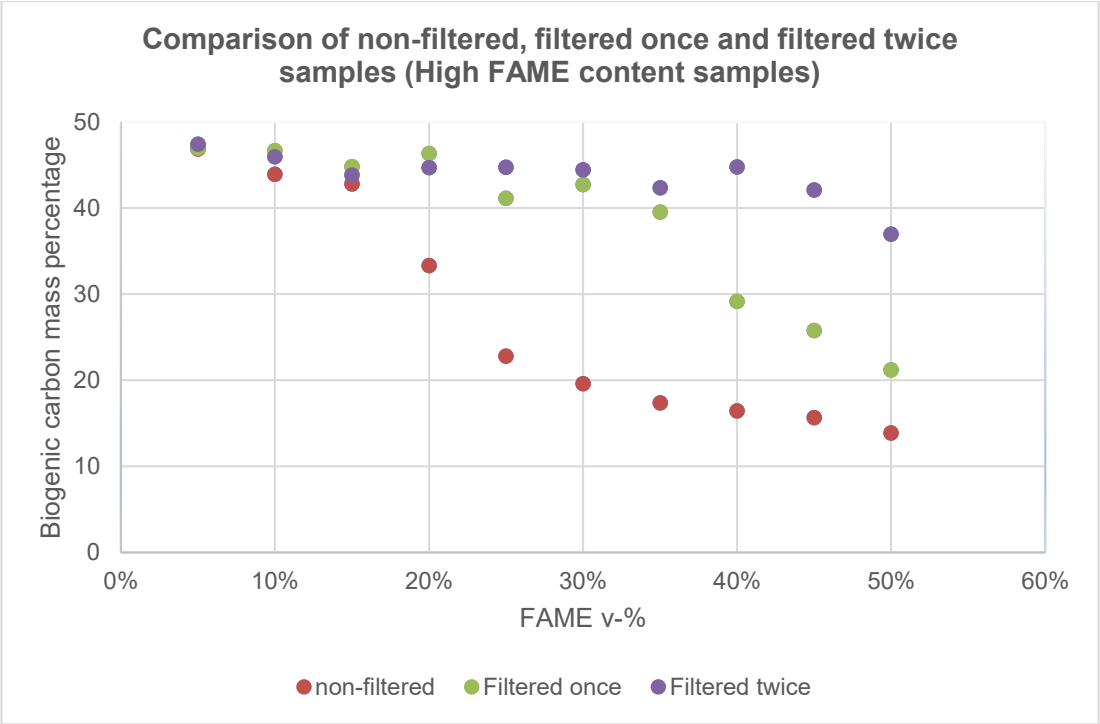

Figure 22. Comparison of samples with high concentration of FAME that are non-filtered, filtered once and samples with high concentration of FAME.

5.2.2 Precision

Precision was used to evaluate the results of samples with low percentages of FAME that were filtered. Each sample (from CBM-12 to CBM-16) was filtered once before being measured twice in a liquid scintillation counter. Table 11 (p.43) shows the average, standard deviation, and relative standard deviation of each sample's results. The standard deviation of filtered samples was calculated using the same formula as non-filtered samples.

Table 11. Averages, standard deviations, and relative standard deviations of low concentration samples that are filtered (CBM-12 to CBM-16).

sample name	FAME v%	Average	Standard deviation	RSD
CBM-12	4 %	47,2075	0,5923	1,2547
CBM-13	3 %	48,2237	0,5943	1,2323
CBM-14	2 %	48,1384	0,3414	0,7092
CBM-15	1 %	48,1412	0,0005	0,0011
CBM-16	0,50 %	48,1413	0,1100	0,2285

Relative standard deviation increases from the samples with the greatest concentration of FAME to the samples with the lowest concentration of FAME, as expected. Filtered samples, on the other hand, have a lower relative standard deviation than non-filtered samples. Compared to the averages of filtered, non-filtered sample's averages are better (far closer to reference values) and more constant. This simply illustrates that by filtering the color from FAME samples, color quench in FAME samples may be reduced. Precision improves when FAME concentration in the sample increases. However, as it was discovered between samples CBM-15 (1 percent FAME) and CBM-16 in non-filtered samples, relative standard deviation of filtered samples starts to increase when the percentage of FAME in sample is below 1 % as well, which means precision from samples with 2 % of FAME to with higher concentration. Comparison of filtered and non-filtered samples with low percentage of FAME is illustrated in Figure 23 (p. 44).

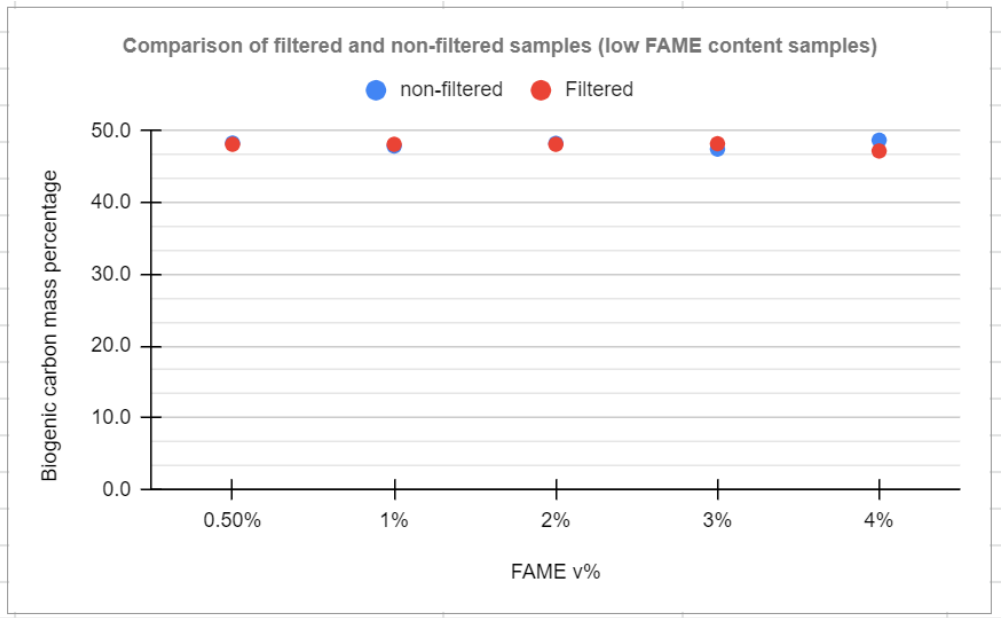

Figure 23. Comparison of filtered and non-filtered low FAME content samples

5.3 CFM series

5.3.1 Trueness

Results of CFM samples that were measured in ASM and averages of results of samples measured in the liquid scintillation counter were and used to evaluate trueness. Deviations from the true value and percentage deviations were calculated from the averages.

Table 12. Relative deviations between LSC measurements for CFM samples and reference measurements (AMS)

Sample name	GTL %	Measured in LSC	True value (Measured in AMS)	deviation from the true value (Bias)	Relative deviation (%)
CFM-2	5 %	47.648	49.020	1.372	2.799
CFM-4	15 %	48.577	52.800	4.223	7.998
CFM-8	35 %	49.839	50.540	0.701	1.387
CFM-10	45 %	50.775	50.780	0.005	0.011

From CFM samples CFM-4 has a slightly higher reference result and relative deviation than other samples. This might be due to a variety of factors, one of which could be a random error. The biogenic carbon mass percentage of the reference sample is much higher than the sample measured in the liquid scintillation counter, which is likely because the bio content calculations of the liquid scintillation counter samples used the values of the atmosphere's radiocarbon activity in 2020 (table1; p.10), resulting in slightly lower bio-percentages. It is also possible that there was not sufficient data since reference samples were only measured once. Apart from CFM-4, it can be observed that trueness improves as the percentage of GTL in the sample increases.

5.3.2 Precision

For CFM samples, precision was evaluated using the standard deviation and relative standard deviation (RSD) and average of sample's biogenic carbon mass percentage values. The deviations and averages are summarized in Table 13.

Table 13. Averages, standard deviations, and relative standard deviations of low CFM samples

Sample name	GTL v-%	Average	Standard deviation	RSD
CFM-1	0 %	47.745	0.190	0.004
CFM-2	5 %	47.648	0.495	0.004
CFM-3	10 %	48.564	0.607	0.010
CFM-4	15 %	48.577	0.542	0.012
CFM-5	20 %	49.020	0.357	0.011
CFM-6	25 %	49.095	0.543	0.007
CFM-7	30 %	49.264	0.502	0.011
CFM-8	35 %	49.839	0.755	0.010
CFM-9	40 %	49.417	0.593	0.015
CFM-10	45 %	50.775	0.296	0.012
CFM-11	50 %	50.766	0.307	0.006

The CFM samples' relative standard deviation is quite low and almost constant, as predicted given the sample's biogenic carbon mass %. This indicates that CFM samples have a good level of precision. Figure 24 illustrates CFM sample's biogenic carbon mass percentage.

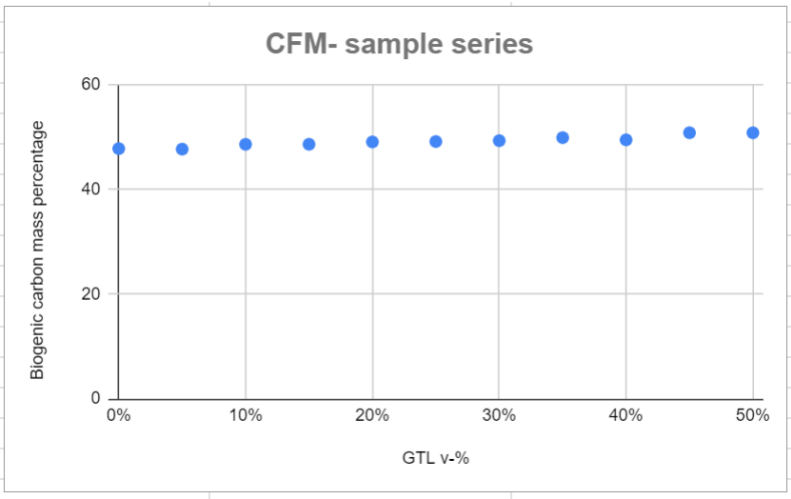

Figure 24. CFM sample's biogenic carbon mass percentage. Measured in liquid scintillation counter.

6 Summary

The purpose of the thesis was to develop a method for the determination of the biogenic content of carbon using Liquid Scintillation Counter (LSC) for samples of changing diesel-type matrix. The method determines the proportion of radiocarbon in a fuel sample thereby the blending rations of biofuel can be calculated. The quantity of renewable diesel in a fuel mixture may be determined using conventional analytical methods used to identify chemically different components using Liquid Scintillation Counting (LSC) and Accelerator Mass Spectrometry (AMS) to determine biogenic content. Biogenic proportion can be determined due to the decomposition of radiocarbon. Radiocarbon 14 (^{14}C) is a radioactive isotope of carbon that is unstable.

For this thesis, two series of samples were prepared to evaluate the method for determining the biogenic content of bio carbon using a liquid scintillation counter. These

series were changing biobased sample matrix (CBM) and changing fossil sample matrix (CFM). Eleven samples were included in each series. Due to the strong color of FAME in the CBM samples, the color quench during the measurements was quite strong. Because of this, five additional samples with low FAME content were added to the CBM series after the first measurement of CBM samples. The liquid scintillation counter was used to measure each sample multiple times. Additionally, in total 15 samples were sent to the external AMS laboratory of University of Helsinki for the reference measurements.

The liquid scintillation counter method's linearity and accuracy were evaluated throughout the validation process. For the LSC method the linear model is good fit for CBM samples with low FAME content but is not a good predictor of CBM samples with high FAME content. The reason for this is that LSC is not completely capable when it comes to bio-content measurement of samples containing FAME due to its containing color.

It was noticed that results worsen for samples with FAME content of higher than 5 %. CBM samples containing more than 5 % FAME show lower biogenic carbon mass percentage results due to strong color quench that take place during sample measurement in a liquid scintillation counter. CBM-2 (5 % FAME) measured in a liquid scintillation counter gives a biogenic carbon mass percentage of 46.8, same samples measured in accelerator mass spectrometry (reference) gives the result of 49.06. Since diesel method has an extended measurement uncertainty of ±5 % (±2.5) therefore taking into consideration the actual value measured with AMS, the result of samples with 5 % of FAME falls well within that range which is not the same for samples with FAME content higher than 5 %.

It was discovered that the color quench during bio-content measurement in LSC is reduced by filtering color from samples containing FAME, and therefore biogenic carbon mass percentage values improve. CBM samples with a high percentage of FAME were filtered once and twice before being measured. When comparing the results of filtered once samples and non-filtered samples, a substantial difference could be noticed (Figure 20, p.40). Biogenic carbon mass percentage results of samples filtered twice before measured (Figure 21, p. 41) improved significantly than samples that were filtered once. A Significant difference was discovered for samples with concentration of FAME higher

than 15 %. When analyzing the accuracy for CBM samples it was discovered that for both filtered and non-filtered samples, trueness is weaker for samples with higher concentration of FAME (over 5 %) and it improves from samples with a high to low concentration of FAME. Precision on the contrary improves from lower to higher concentrations for filtered and non-filtered samples.

For CFM samples trueness improves as the percentage of GTL in the samples decreases. Relative standard deviation for CFM samples is quite low and almost constant, this indicates that CFM samples have a good level of precision. Biogenic carbon mass percentage of samples increases as GTL percentage in samples increases as well. During the measurements, it was discovered that the tSIE values of the CFM samples (Table 19, appendix 6) are fairly low at low bio-concentrations and increase with increasing bio-content. tSIE values also increase when the GTL percent of samples increases. The external standard spectrum's attenuation parameters dropped, as did the sample's bio-content. This is mostly because CFM series samples contain fossil diesel, which has a light-yellow color (Figure 12; p.26), and its amount increases as GTL's amount decreases in samples, resulting in an increase in sample color and a reduction in sample bio content.

tSIE values for unfiltered samples are very low in comparison to the ideal tSIE value for samples, and their values and bio content values worsen as FAME percentage in samples increase. The tSIE value worsen for unfiltered samples when FAME content is higher and lower than 4 % in sample. tSIE and bio content values of filtered samples improve after sample's filtration compared to samples that are not filtered and the values improve as FAME content decreases in samples. For samples that were filtered twice before measurement, their tSIE and bio content values improve compared to samples filtered just once, and the values improve as FAME content of samples decreases. Therefore, the more samples are filtered before measurement, the higher the tSIE and bio content values are. tSIE values of all samples measured in liquid scintillation counter are found in appendices 1 to 7.

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Appendix 1. ResultS of CBM high FAME content samples measured in LSC

Table 14. CBM, High FAME content

Sample name	Sample mass (g)	dpm	cpm	tSIE	Efficiency (E)	Lumines-cence	biogenic carbon (m%)
GTL	8.0024	3.92	3.16	813.93	80.612	5	-0.172
FAME	8.0042	8.53	2.53	50.81	29.660	15	4.849
HVO	8.0011	97.33	76.49	816.77	78.588	1	101.621
CBM-1	8.0046	49.49	39.85	816.77	80.521	1	49.464
CBM-2	8.0048	47.08	33.33	220.35	70.794	2	46.838
CBM-3	8.0046	44.38	31.06	220.35	69.986	2	43.898
CBM-4	8.0052	43.38	17.61	84.64	40.595	3	42.806
CBM-5	8.0015	34.66	12.13	67.3	34.997	3	33.325
CBM-6	8.0092	25.02	8.9	94.76	35.572	5	22.795
CBM-7	8.0082	22.08	7.08	46.51	32.065	4	19.597
CBM-8	8.0071	20.03	5.71	38.95	28.507	6	17.368
CBM-9	8.0001	19.17	4.89	37.84	25.509	7	16.450
CBM-10	8.0013	18.44	4.41	32.92	23.915	8	15.651
CBM-11	8.0044	16.8	4.02	32.98	23.929	8	13.857

Appendix 2: Results of CBM low FAME content samples measuredn in LSC

Table 15. CBM, Low FAME content.

Sample name	Sample mass (g)	dpm	cpm	tSIE	efficiency (E)	Luminesc-ence	biogenic carbon (m %)
CBM-12	8.0018	48.87	35.74	254.62	73.133	2	48.808
CBM-13	8.0032	47.06	36.5	309.75	77.561	2	46.827
CBM-14	8.0086	47.87	38.91	395.99	81.283	1	47.674
CBM-15	8.0027	48.34	40.44	524.26	83.657	1	48.224
CBM-16	8.0096	49.01	40.91	626.06	83.473	1	48.908
CBM-12	8.003	49.3	36.07	254.41	73.164	2	49.268
CBM-13	8.0073	47.53	36.89	310.58	77.614	1	47.312
CBM-14	8.0037	49.2	39.92	390.32	81.138	1	49.155
CBM-15	8.0078	47.78	39.97	519.61	83.654	1	47.581
CBM-16	8.0095	48.77	40.71	631.06	83.473	1	48.648
CBM-12	8.0032	46.14	34.81	278.68	75.444	2	45.824
CBM-13	8.0061	48.84	37.67	301.25	77.129	1	48.746
CBM-14	8.0016	47.99	39.01	395.97	81.288	1	47.850
CBM-15	7.9986	48.05	40.2	516.33	83.663	1	47.935
CBM-16	8.0075	48.63	40.61	619.23	83.508	1	48.509
CBM-12	8.0038	48.41	35.32	252.27	72.960	2	48.293
CBM-13	8.0091	48.11	37.36	311.46	77.655	2	47.932
CBM-14	8.0012	48.04	39.02	393.08	81.224	2	47.907
CBM-15	8.0085	48.09	40.23	523.04	83.656	1	47.914
CBM-16	8.0005	48.15	40.2	621.19	83.489	1	48.032
CBM-12	8.0089	48.12	34.97	248.55	72.672	2	47.944
CBM-13	8.0069	48.16	37.25	305.68	77.346	2	48.001
CBM-14	7.9998	47.65	38.71	394.25	81.238	1	47.491
CBM-15	8.0052	48.32	40.42	521.59	83.651	1	48.186
CBM-16	8.0052	47.53	39.69	620.49	83.505	1	47.326

Appendix 3: Results of CBM high FAME content samples that are filtered once and measured in LSC

Table 16. CBM, High FAME content filtered once

sample name	Sample mass (g)	dpm	cpm	tSIE	efficiency (E)	Luminesc-ence	biogenic carbon (m%)
CBM-2.filt	7.9972	47.13	39.28	668.58	83.344	1	46.941
CBM-3.filt	8.0017	46.91	38.39	415.29	81.838	2	46.673
CBM-4.filt	8.0062	45.21	33.88	273.34	74.939	2	44.793
CBM-5.filt	8.0054	46.63	29.06	162.74	62.320	2	46.344
CBM-6.filt	8.0041	41.82	25.96	161.49	62.076	2	41.113
CBM-7.filt	8.0091	43.32	18.46	90.92	42.613	3	42.717
CBM-8.filt	8.0082	40.38	15.7	79.36	38.881	3	39.521
CBM-9.filt	8.0034	30.85	10.06	59.91	32.609	4	29.166
CBM-10.filt	8.0065	27.76	8.45	53.1	30.439	4	25.788
CBM-11.filt	8.0003	23.53	6.44	43.5	27.369	5	21.201

Appendix 4. Results of CBM high FAME content samples that are filtered twice and measured in LSC

Table 17. CBM, High FAME content filtered twice

Sample name	Sample mass (g)	dpm	cpm	tSIE	efficiency (E)	Luminesc-ence	biogenic carbon (m%)
CBM-2.filt.X2	8.0066	47.6	39.57	686.43	83.130	1	47.392
CBM-3.filt.X2	7.9993	46.23	38.68	507.99	83.668	1	45.946
CBM-4.filt.X2	8.0038	44.31	36.49	432.99	82.351	2	43.826
CBM-5.filt.X2	8.0090	45.15	35.24	319.03	78.050	2	44.710
CBM-6.filt.X2	8.0098	45.18	31.76	223.74	70.296	2	44.737
CBM-7.filt.X2	8.004	44.86	29.33	178.55	65.381	2	44.424
CBM-8.filt.X2	8.0033	42.97	26.23	156.23	61.042	2	42.370
CBM-9.filt.X2	8.0093	45.2	21.39	105.53	47.323	2	44.762
CBM-10.filt.X2	8.0069	42.74	18.17	90.61	42.512	3	42.098
CBM-11.filt.X2	8.0075	38.04	14.27	75.09	37.513	3	36.977

Appendix 5. Results of CBM low FAME conten samples that are filtered once and measured on LSC

Table 18. CBM, Low FAME content, Filtered

Sample name	Sample mass (g)	dpm	cpm	tSIE	efficiency (E)	Lumines-cence	Biogenic carbon (m%)
CBM-12	8.0023	47.02	39.23	624.92	83.433	1	46.789
CBM-13	8.0004	47.94	39.86	684.98	83.146	1	47.804
CBM-14	8.0039	48.49	40.23	700.8	82.966	1	48.380
CBM-15	8.0038	48.27	23.61	774.7	48.912	1	48.141
CBM-16	8.0035	48.34	39.64	781.06	82.002	1	48.219
CBM-12	8.0092	47.83	39.94	617.54	83.504	1	47.626
CBM-13	8.0035	48.73	40.49	690.38	83.090	1	48.644
CBM-14	8.0061	48.06	39.6	746.91	82.397	1	47.897
CBM-15	8.0070	48.29	39.37	794.39	81.528	1	48.142
CBM-16	8.0023	48.19	39.3	793.35	81.552	1	48.064

Appendix 6: Results of CFM samples measured in LSC.

Table 19. CFM

Sample name	Sample mass (g)	dpm	cpm	tSIE	efficiency (E)	Lumines-cence	biogenic carbon (m%)
CFM-1	8.0076	48.04	39.45	770.61	82.119	1	47.865
CFM-2	8.0074	47.45	38.9	781.91	81.981	1	47.224
CFM-3	8.0085	48.15	39.48	781.69	81.994	1	47.979
CFM-4	8.0024	48.92	40.18	769.33	82.134	1	48.858
CFM-5	8.0003	48.85	39.94	789.23	81.760	1	48.796
CFM-6	8.0000	48.55	39.81	780.91	81.998	1	48.471
CFM-7	8.0060	49.21	40.05	797.47	81.386	1	49.150
CFM-8	8.0092	49.9	40.82	787.92	81.804	1	49.880
CFM-9	8.0092	48.95	39.77	800.4	81.246	1	48.846
CFM-10	8.0022	50.94	41.12	812.3	80.722	1	51.061
CFM-11	8.0025	50.59	35.74	829.95	70.646	1	50.677
CFM-1	8.0094	48.03	39.39	779.26	82.011	1	47.843
CFM-2	7.9993	48.29	39.41	792.27	81.611	1	48.192
CFM-3	8.0016	49.22	40.18	791.97	81.633	1	49.190
CFM-4	8.0026	48.09	39.17	795.77	81.451	1	47.953
CFM-5	8.0094	49.49	40.33	795.03	81.491	1	49.432
CFM-6	8.0035	49.48	40.24	798.71	81.326	1	49.461
CFM-7	8.0015	49.79	40.17	813.38	80.679	1	49.812
CFM-8	8.0008	49.1	39.82	803.81	81.100	1	49.065
CFM-9	8.0079	50.03	40.37	813.33	80.692	1	50.030
CFM-10	8.0043	50.41	40.86	804.65	81.055	1	50.469
CFM-11	8.004	50.45	40.2	836.16	79.683	1	50.514
CFM-1	8.0063	47.72	39.22	764.71	82.188	1	47.525
CFM-2	8.0059	47.72	39.15	776.41	82.041	1	47.528
CFM-3	8.0053	48.63	39.93	770.37	82.110	1	48.523
CFM-4	8.0012	48.97	40.04	789.09	81.764	1	48.921
CFM-5	8.0096	48.94	39.93	790.84	81.590	1	48.832
CFM-6	8.0064	49.4	39.97	808.25	80.911	1	49.354

CFM-7	8.0003	48.88	39.54	808.81	80.892	1	48.829
CFM-8	8.0082	50.53	40.53	823.93	80.210	1	50.573
CFM-9	8.0081	49.43	40.19	799.06	81.307	1	49.376
CFM-11	8.0076	50.73	40.81	818.96	80.445	1	50.794
CFM-10	8.0017	50.98	41.07	816.19	80.561	1	51.108

Appendix 7: Results of refference samples measured in AMS

Table 19. Results of refference samples measured in AMS

Sample name	Biogenic carbon (m%)
Fossil diesel	0.89
GTL	0.01
HVO	106.56
FAME	102
CBM-2	47.3
CBM-4	50.98
CBM-8	47.91
CBM-10	47.73
CFM-2	49.02
CFM-4	52.8
CFM-8	50.54
CFM-10	50.78
CBM-2	50.82
CBM-12	49.66
CBM-13	50.91
CBM-14	48.38
CBM-15	49.13
CBM-16	59.42