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INTERCOMPARISON EXERCISE ON FUEL SAMPLES FOR DETERMINATION OF BIOCONTENT RATIO BY ^{14}C ACCELERATOR MASS SPECTROMETRY

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ABSTRACT. The method of determining the biobased carbon content in liquid fuel samples is standardized, but different laboratories use different protocols during sample preparation and perform the measurements using different machines. The accelerator mass spectrometry (AMS) laboratories use different combustion, preparation, and graphitization methods for the graphite production for the spectrometric measurements. As a result, the intercomparison between the laboratories is inevitable to prove precision and accuracy and to demonstrate that the results are comparable. In this study, we present the results of an intercomparison campaign involving three ^{14}C accelerator mass spectrometry laboratories. Five samples were used in the measurement campaign, including two biocomponents (fatty acid methyl ester, hydrotreated vegetable oil), one fossil component (fossil diesel), and two blends (mixtures of fossil and biocomponent with 90–10% mixing ratio) in the laboratories of CEDAD (Italy), ETH (Switzerland), and INTERACT (Hungary). The results presented by the laboratories are comparable, and all three laboratories could determine the biobased carbon content of the samples within 1% relative uncertainty, which is acceptable in the scientific, economic, and industrial fields for biocomponent determination.

KEYWORDS: AMS, biobased carbon content, liquid fuel, radiocarbon.

INTRODUCTION

The European Union (EU) began implementing biofuel-related targets in 2003 (European Parliament 2003). The Biofuel Directive set indicative biofuel penetration targets of 2% by the end of 2005 and 5.75% by the end of 2010. In 2009, the EU Commission passed two major directives supporting the increased use of renewable fuels extending to 2020. The Renewable Energy Directive (RED) mandates that 20% of all energy usage in the EU, including at least 10% of all energy in road transport fuels, be produced from renewable sources by 2020. Alongside the RED, an amended Fuel Quality Directive (FQD) was passed requiring that, by 2020, the road transport fuel mix in the EU should be 6% less carbon intensive than a fossil diesel and gasoline baseline.

The increasing amount and demand of used biobased fuel components require reliable and independent measurement techniques of the biocontent ratio determinations in blends. It is not only a scientific interest, but also an economic demand (Oinonen et al. 2010; Deneyer et al. 2018; Varga et al. 2018; Delli Santi et al. 2021). Renewable components in the fuel industry, such as biofuels, are generally made by biological processing of recent organic materials. Based on classical analytical techniques, such as chromatography methods, it is

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difficult to distinguish the fossil (petroleum based) and biogenic (recent) component of the mixed fuel samples because the physical and chemical properties of these materials are quite similar. That is why they can be applied together in the same engine as well, but the analytical differentiation within the mixture is not trivial (Deepanraj et al. 2011; Lawrence et al. 2011; Varga et al. 2018).

The carbon content of the fuel materials is generally high, so the measurement of the carbon isotopes composition, for the purpose of biocontent analysis, can be representative of the whole sample biocontent ratio as well (Dijs et al. 2006; Varga et al. 2018; Haverly et al. 2019). Laser-based radiocarbon measurements have begun to gain ground nowadays, but the precision and accuracy are better in the case of the accelerator mass spectrometry (AMS) method, and the necessary amount of sample is also lower for AMS measurement, however the laser-based ^{14}C determination could be a cost-effective way for the industry in the future (Genoud et al. 2015, 2019; Delli Santi et al. 2021). The liquid scintillation counting (LSC) based method could be cheaper than the AMS, but burdened with many difficulties, such as quenching in the fuel blend samples which are not transparent liquids (Doll et al. 2017; Krajcar Bronić et al. 2017). Radiocarbon-based biocontent ratio measurement is also used for the determination of the biocomponent ratio in plastics and other materials that can be produced also from bio and fossil sources (Quarta et al. 2013; Palstra and Meijer 2014; Santos et al. 2019; Rogers et al. 2021).

Determination of the biological component ratio by the radiocarbon (^{14}C) method has been standardized (ASTM D6866 2020). Using this standard method, the $^{14}\text{C}/^{12}\text{C}$ isotopic ratio can be determined by AMS (Norton et al. 2007; Oinonen et al. 2010; Culp et al. 2014; Funabashi et al. 2014; Varga et al. 2018; Haverly et al. 2019). Although the method is standardized, different laboratories use different preparation methods and AMS instruments made by different manufacturers for the measurement. Therefore, intercomparison activities are required for the comparison and demonstration of compliance of the different measurement protocols at AMS laboratories worldwide (Rozanski and Stichler 2006; Haverly et al. 2019; Wacker et al. 2020; Quarta et al. 2021).

Our aim was to involve three separate laboratories in the presented intercomparison campaign for the determination biocontent of unknown bio-, fossil, and mixed-fuel samples, in the framework of the IAEA (International Atomic Energy Agency) CRP (Coordinated Research Projects): Enhancing Nuclear Analytical Techniques to Meet the Needs of Forensic Sciences. Our AMS ^{14}C study shows the intercomparison of the results data of two biofuel, one fossil fuel, and two blends from these materials. The samples were measured at (a) the Centre of Applied Physics, Dating and Diagnostics (CEDAD), University of Salento, Lecce, Italy, (b) ETH Zürich, Department of Earth Sciences, Ion Beam Physics laboratory, Zürich, Switzerland, and (c) Institute for Nuclear Research, International Radiocarbon AMS Competence and Training (INTERACT) Center, Debrecen, Hungary. The samples were provided by the Hungarian oil company, MOL Plc.

MATERIALS AND METHODS

Fuel Samples

Five fuel samples were processed in the three participating laboratories. A fatty acid methyl ester (FAME) (Vyas et al. 2010) sample and hydrotreated vegetable oil (HVO) (Aatola et al. 2010; Dimitriadis et al. 2018) were used as modern biocomponent, and “EVO” fossil

Table 1 Properties of processed fuel samples.

No.	Name	Description
1.	FAME	Pure (100%) fatty acid methyl ester (FAME); basically fresh organic material, but during the methyl-addition, a small quantity of fossil carbon was added (density at 15°C kg/m ³ : ~885 kg/m ³ (Aatola et al. 2008))
2.	HVO	Pure (100%) hydrotreated vegetable oil (HVO); basically fresh organic material (density at 15°C kg/m ³ : ~780 kg/m ³ (Aatola et al. 2008))
3.	Mixed 1	Mixture of 10 mL FAME (sample #1) and 90 ml fossil EVO (sample #5).
4.	Mixed 2	Mixture of 10 mL HVO (sample #2) and 90 ml fossil EVO (sample #5).
5.	EVO	Pure (100%) fossil liquid fuel (EVO); basically only fossil natural oil, ¹⁴ C free, expected is: 0.0 pMC (density at 15°C kg/m ³ : ~835 kg/m ³ (Aatola et al. 2008))

fuel was used as pure fossil material for creating two different mixtures (Mixed 1 and Mixed 2) (Table 1). 10 mL from these samples was delivered to each laboratory in glass vials for AMS analysis. The laboratories had no knowledge about the ¹⁴C content of the samples, only that the samples were bio and fossil fuels or blends of the two components.

The mixed samples were chosen by the recent regulations and general biocomponent ratio in fuels in Europe and Hungary. In our former study, a wider range of mixed samples were tested, but this recent study focuses only on the ~10% biocomponent ratio (Varga et al. 2018).

Sample Processing at CEDAD

About 5 mg of bio-fuel samples without any preliminary chemical processing were frozen and vacuum sealed in quartz tubes together with CuO and silver wool. The samples were then combusted at 900°C for 8 hr in a muffle oven. The released CO₂ was recovered by breaking the quartz tubes under vacuum, cryogenically purified and reduced to graphite at 600°C by using hydrogen as reducing agent and iron powder as catalyst.

All the samples yielded ~1 mg of graphite which was then pressed in the aluminum cathodes of the AMS system (3 MV Tandatron™ Mod. HVEE 4130HC) for the measurement of the isotopic ratios (Calcagnile et al. 2019). Measured ¹⁴C/¹²C ratios were then corrected for mass fractionation by using the δ¹³C term measured online with the AMS system and for machine and chemical processing background. Uncertainty on measured isotopic ratios was calculated by considering both the scattering of the 10 repeated determinations performed on the same sample and the radioisotope counting statistics (Calcagnile et al. 2005).

Sample Processing at ETH

At the ETH laboratory, 2–3 mg of fuel samples was weighed into 9 mm Vycor tubes, which were filled with CuO wires and precooked at 950°C. The tubes were sealed under vacuum and placed a muffle furnace for 2 hr to combust at 950°C. The ampoules were then cracked under vacuum and the CO₂ cryogenically recovered and transferred to 6 mm diameter tubes, which allowed for dividing the CO₂ to multiple tubes (sub-samples). These were then cracked, and CO₂ was transferred to the AGE graphitization system using He flow. Graphite samples

were pressed into the targets for analysis with LIP MICADAS (Synal et al. 2007). For the data evaluation the Bats AMS software was used (Wacker et al. 2010a).

Sample Processing at INTERACT

At the INTERACT the fuel samples were not chemically prepared before the combustion. From the fuel samples, 4–5 mg was weighed by a glass capillary into a borosilicate combustion tube already containing ~300 mg MnO₂ powder as oxidation reagent. Then the tubes were cooled by mixture of dry ice and alcohol slush (to –70°C) to avoid fuel evaporation during glass sealing performed under vacuum by flame. The sealed fuel samples were combusted off-line at 550°C, 24 hr in a muffle furnace (Janovics et al. 2018; Varga et al. 2018). The ampoules containing the combusted fuel samples were then cracked under vacuum and the produced CO₂ was cryogenically recovered and transferred to the graphitization ampoules in a gas handling line (Janovics et al. 2018). At INTERACT the sealed tube graphitization method was used to convert the purified CO₂ to graphite by Zn reduction method (Rinyu et al. 2013). A MICADAS type accelerator mass spectrometer was used for the determination of carbon isotopic composition (Wacker et al. 2010b; Molnár et al. 2013). For the data evaluation the Bats AMS software was used (Wacker et al. 2010a).

Biocontent Calculation

The measured, raw ¹⁴C activity (pMC) data were corrected by the value of the measured value of the fossil (EVO) component. (pMC_{EVO})

$$\text{pMC}_{\text{EVO}} = \text{pMC}_s - \text{pMC}_f \quad (1)$$

where pMC_s is the measured ¹⁴C activity (pMC) value of the biocomponent or mixed sample and the pMC_f is the measured ¹⁴C activity (pMC) value of the fossil (EVO) component.

The biobased carbon content (C_b) was calculated by the standard method (ASTM D6866 2020):

$$C_b = \left(\frac{\text{pMC}_s}{\text{pMC}_{\text{ref}}} \right) \times 100 \quad (2)$$

where pMC_s is the measured ¹⁴C activity (pMC) value of sample, and the pMC_{ref} is the ¹⁴C activity (pMC) value of the reference, biocomponent sample. The C_b can be calculated using the pMC_{EVO} to use the fossil component corrected ¹⁴C activity (pMC) value instead of the pMC_s for the calculation of biobased carbon content (C_{bEVO}).

The actual biobased carbon (C_a), according to the mass balance between the applied bio component and the fossil matrix, may differ from the standardized Biobased carbon content calculation. C_a was calculated by the following equation:

$$C_a = \left(\frac{C_{\text{bio}} \times 100}{C_m} \right) \quad (3)$$

where C_{bio} is the carbon content (g) of the biocomponent (FAME or HVO) and C_m is the carbon content (g) of the mixed sample. The carbon content was determined at the

Table 2 Input data for Equation (3).

Properties	Value	Unit
Carbon content of 10 ml FAME component in Mixture 1 (C_{bio})	6.873	g
Carbon content of 10 ml HVO component in Mixture 2 (C_{bio})	6.638	g
Carbon content of 90 ml fossil (EVO) component in Mixture 1 and Mixture 2 (C_{m})	65.70	g
$m_{\text{Mixture 1}}$	72.57	g
$m_{\text{Mixture 2}}$	72.34	g
ρ_{FAME} (Aatola et al. 2008)	0.88	g/mL
ρ_{HVO} (Aatola et al. 2008)	0.78	g/mL
ρ_{EVO} (Aatola et al. 2008)	0.84	g/mL
Carbon content FAME (measured at the INTERACT)	78.1	%
Carbon content HVO (measured at the INTERACT)	85.1	%
Carbon content FOSSIL (measured at the INTERACT)	86.9	%

INTERACT after the purification of the CO_2 gas, measured in a known volume by pressure transducer (Janovics et al. 2018). The carbon content of the bio and fossil components for the calculation of carbon content of the mixed samples were determined by using the literature data of the density of bio and fossil components (Aatola et al. 2010; Varga et al. 2018), measured carbon content of bio and fossil sources that was measured in the INTERACT (Janovics et al. 2018; Varga et al. 2018) and mass percentage of the blends measured at the laboratory of MOL by gravimetric method with a Sartorius 1702MP8 Electronic Analytical Balance (precision ± 0.1 mg). Table 2 presents the input data for Equation 3.

Simple difference from the actual biobased (C_{a}) content was calculated between the measured and actual biobased carbon content (C_{diff}):

$$C_{\text{diff}} = C_{\text{b}} - C_{\text{a}} \quad (4)$$

Expected ^{14}C activity of the mixture is obtained by combining Equations (2) and (3):

$$\text{pMC}_e = \left(\frac{C_{\text{bio}} \times \text{pMC}_{\text{ref}}}{C_{\text{m}}} \right) \quad (5)$$

where C_{bio} is the carbon content (g) of the biocomponent (FAME or HVO) and pMC_{ref} is the measured ^{14}C activity (pMC) value of the biological material in the mixture, C_{m} is the carbon content of the mixture.

RESULTS AND DISCUSSION

Five fuel sample were measured in each laboratory by accelerator mass spectrometry method. Then, based on the processing and AMS measurement data, biobased carbon content was calculated for the mixed fuel samples. The actual (C_{a}), calculated biobased content (C_{b}), measured and expected ^{14}C activity (pMC) of the fuel samples are shown in the Table 3. The Table 3 also show the calculated difference of the actual biobased content and show the data calculated by EVO corrected ^{14}C activity (pMC) values. The raw measurement data and calculations are shown in the Supplementary Material S1 file.

Table 3 Measured carbon content, expected and measured mean radiocarbon ratio (pMC), calculated actual biobased carbon content, EVO corrected biobased carbon content calculated by the AMS measurements and the difference between actual (C_a) and calculated biobased carbon content (C_b).

Sample	Measured carbon content (%) ^a	pMC _e (pMC _e , %)	Mean measured pMC	C_a (%)	C_b (%)	C_{bEVO} (%)	C_{diff}	C_{diff} by C_{bEVO}
FAME	0.78	~100 ^b	96.68 ± 0.19					
HVO	0.85	~100 ^b	102.49 ± 0.12					
Mixed 1	0.86	9.13	9.36 ± 0.31	9.47	9.68 ± 0.31	9.37 ± 0.18	0.20 ± 0.31	-0.11 ± 0.18
Mixed 2	0.87	9.37	9.96 ± 0.23	9.18	9.72 ± 0.22	9.42 ± 0.13	0.40 ± 0.24	0.24 ± 0.13
EVO	0.87	0 ^c	0.34 ± 0.14					

^aThe carbon content of the samples was measured in the INTERACT laboratory by the method described in Janovics et al. (2018) and Varga et al. (2018).

^bThe expected ¹⁴C activity of biogenic component is around 100 pMC, this value was not calculated by Equation (5), but the expected value depends on the year of the production of the biological material

^cThe expected ¹⁴C activity of fossil component is 0 pMC, due to the long geological storage, the ¹⁴C content of the fossil materials is completely decayed away. This value was not calculated by Equation (5).

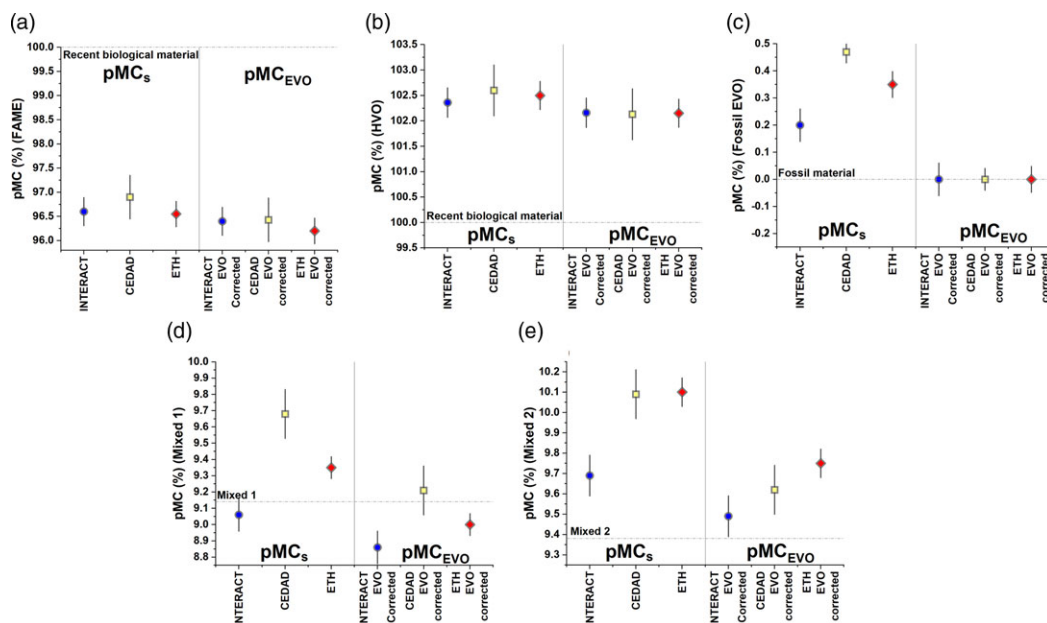


Figure 1 Results of the AMS measurements in the three different laboratories. Plots show pMC data of (a) FAME, (b) HVO, (c) EVO, (d) Mixed 1, and (e) Mixed 2 fuel samples and blends.

For the FAME and HVO biofuel materials the mean radiocarbon contents (pMC) measured in the three laboratories were 96.68 ± 0.19 and 102.49 ± 0.12 pMC, respectively (Table 3; Figure 1a and 1b). There is a good agreement among the individual data for each of the mentioned group (within one standard deviation). The recent organic materials ^{14}C activity should be 100 pMC in the year of 2020 by the standard, but these materials can slightly be older, thus contain a bit more radiocarbon, inheriting from the radiocarbon bomb-peak (Hua and Barbetti 2004; Turney et al. 2018; Kontul' et al. 2020). Our samples were produced in 2018, that is why the HVO samples have higher radiocarbon content than 100 pMC. The results of the FAME samples are a bit lower than 100 pMC, because it contains methyl group originated from fossil material (Holmgren et al. 2007). The mean measured pMC values at the three laboratories are close to the expected 9.13 (Mixed 1) and 9.37 (Mixed 2) pMC values, respectively 9.36 ± 0.31 (Mixed 1) and 9.96 ± 0.23 (Mixed 2) pMC (Table 3; Figure 1c and 1d). The mean difference between the mean measured pMC and pMC_c is 0.24 ± 0.31 (Mixed 1) and 0.59 ± 0.23 (Mixed 2) pMC. The mean difference calculated using the measurement values of the three laboratories is under 0.6 pMC for the Mixed 1 and Mixed 2 samples. Higher than 1 pMC difference was not observed.

The EVO corrected pMC (pMC_{EVO}) values also show good agreement between the three laboratories and the calculated value also close to the expected pMC value of the Mixed 1 and Mixed 2 blended samples (Table 3; Figure 1c and 1d). The mean difference is not higher than 0.3 pMC at the three labs in the case of the EVO corrected pMC values. The mean difference between the mean, EVO corrected pMC and pMC_c is -0.10 ± 0.18 (Mixed 1) and 0.25 ± 0.13 (Mixed 2) pMC in the EVO corrected samples compared to the expected pMC values. It shows the importance of correction by the measured value of the prepared fossil component (EVO), as the deviation from the expected pMC value is less than half after blank correction.

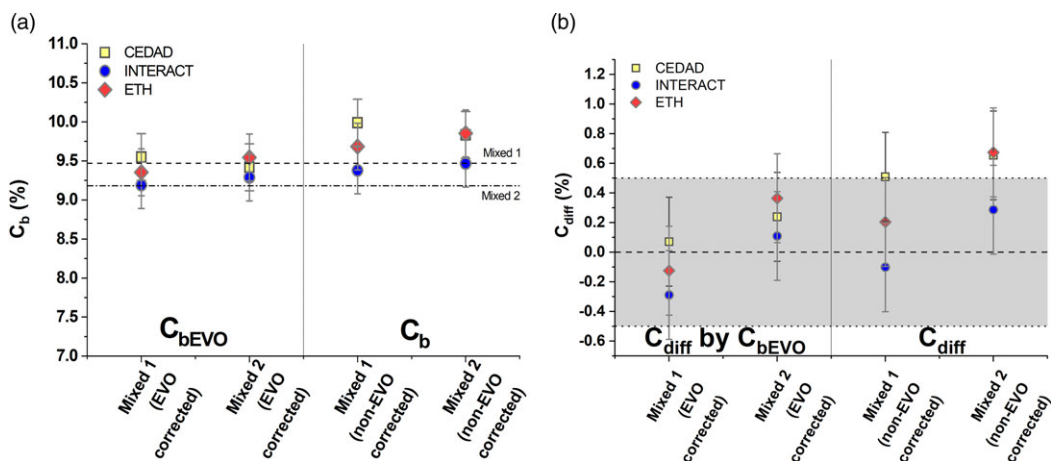


Figure 2 Plot (a) shows the calculated biogenic carbon content of the samples with (C_{bEVO}) and without EVO correction (C_b). Plot (b) shows the difference of the determined bio carbon content of the mixed samples from the actual bio carbon content (EVO corrected (C_{diff} by C_{bEVO}) and non-EVO corrected data (C_{diff}). The gray area shows the $0 \pm 0.5\%$ difference from the actual bio C content.

The mean, calculated biobased carbon contents (C_b) are $9.68 \pm 0.31\%$ (Mixed 1) and $9.72 \pm 0.22\%$ (Mixed 2) without correction, and $9.37 \pm 0.18\%$ (Mixed 1) and $9.42 \pm 0.13\%$ (Mixed 2) with correction by the fossil (EVO) component (C_{bEVO}) (Figure 2a). The highest relative difference from the expected value (C_{diff}) of Mixed 1 sample was 0.51% observed in the non-corrected measurements but the highest difference is only -0.29% after the correction by the fossil component (C_{diff} by C_{bEVO}) (Figure 2b). The highest difference from the expected value (C_{diff}) of Mixed 2 sample was 0.67% observed in the non-corrected measurements, (0.36% after the correction [C_{diff} by C_{bEVO}]) (Figure 2b). These results show that all three participating laboratories could determine the biobased carbon content of the fuel samples within 1% relative uncertainty.

CONCLUSION

Three AMS ^{14}C laboratories were involved in the intercomparison campaign for biobased carbon content measurement (ETH Zürich, CEDAD Lecce, INTERACT Debrecen). The laboratories prepared and measured the samples with different methods and machines to present the robustness, precision, and accuracy of the ^{14}C -based biocomponent ratio measurements. The calculated $^{14}\text{C}/^{12}\text{C}$ ratio (pMC) and biobased carbon content results are in good agreement among the three laboratories and the real, actual biobased content of the distributed samples. All of the laboratories could determine the biobased carbon content within 1%, which shows that the applied methods can meet the most expectations even at the industrial field. The findings based on our intercomparison with three laboratories cannot be generalized for every AMS ^{14}C laboratory, but the precision and accuracy of the presented results are similar to those found in the literature (Oinonen et al. 2010; Krajcar Bronić et al. 2017; Varga et al. 2018; Haverly et al. 2019).

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SUPPLEMENTARY MATERIAL

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