COMPARISON OF TWO DIFFERENT METHODS FOR DETERMINATION OF BIOGENIC FRACTION IN LIQUID FUELS

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INTRODUCTION

Determination of biogenic fraction in liquid fuels by direct measurement of the ^{14}C activity concentration via liquid scintillation counting (LSC) technique has been adopted in few laboratories worldwide. This method is regarded as fast, simple, accurate and sensitive determination procedure for the mass assessment of biogenic fraction in biofuels [1,2]. There are some variations in the calibration techniques used by different laboratories that should be compared by intercomparison measurements. There is a great variety of biogenic matrices in fuels available on the market, so the calibration curves should work well for a variety of bio-components in various fossil fuels matrices.

Two laboratories participated in this study: Laboratory for low radioactivity at the Department of Physics, University of Novi Sad (UNS), Serbia, and Laboratory for low-level radioactivities of the Ruđer Bošković Institute (RBI) in Zagreb, Croatia. UNS performed a two-step method for calibration that is described in detail in [1]. A technique that uses liquids of different colours to construct modern and background calibration curves, MCC and BCC, respectively, by measuring count rates and SQP(E) values of various modern and fossil liquids has been developed at RBI [2,3]. In order to compare these two calibration methods, we used the same set of mixture with the known fractions of the biogenic component.

MATERIAL AND METHODS

Both laboratories used the same type of measuring equipment, Ultra Low Level Liquid Scintillation Spectrometer Quantulus1220 (Wallac Oy,

PerkinElmer). It has low background count rates and a possibility of measurement of quench indicating parameter SQP(E), Spectral Quench Parameter of the External Standard. The SQP(E) represents channel number of 99^{th} percentile of spectrum generated by external standard ^{152}Eu stored in Quantulus. Samples with higher quench level have lower SQP(E) values, which is a consequence of spectra shifting towards lower channels in the presence of quench. SQP(E) values at UNS were measured for each sample for 10 min which is reported to be optimal measurement time for precise quench determination [1], while at RBI 1-minute measurement of SQP(E) preceeded each 30-minute measurement of a sample. Spectra were acquired by WinQ software and evaluated by EasyView.

UNS used UltimaGold F scintillation cocktail and 10 ml:10 ml volume ratio of the sample:scintillation cocktail in plastic vials. Calibration of the instrument was carried out with two commercial fossil fuels with additives for winter and summer season added. FAME (Fatty Acid Methyl Esters) are the most popular and common forms of the biofuels on the global market at the moment [4]. Blends of commercial diesel with winter and summer additives were prepared with biodiesel in volume ratios 99:1 %, 97:3 %, 95:5 %, 93:7 %, 90:10 % and 0:100 % as calibration samples. "Two-step" calibration procedure was used. It demands quench correction curve (efficiency vs. SQP(E) correlation), which enables activity concentration calculation and its dependence on biogenic content in fuel, followed with activity concentration vs. biogenic content in fuel correlation [1].

RBI used 10 ml of UltimaGold F scintillation cocktail mixed with 10 ml of liquid sample in low-potassium glass vials. Several types of fossil fuel, pure benzine and benzene (used as ^{14}C-free background for ^{14}C dating) were used for BCC, and various types of domestic oil (vegetable, sunflower, olive, pumpkin, flax, peanut, corn sprouts), bioethanol and benzene prepared from modern samples were used for MCC construction [2]. The procedure for the unknown sample consists of: 1) measurement of the count rate and the SQP(E) value, 2) calculation of background and modern count rates corresponding to the measured SQP(E) value based on the BCC and MCC curves, respectively, and 3) the ratio of net count rates of the unknown sample and the modern net count rate at the same SQP(E) represents the fraction of the biogenic component in the liquid. The count rate of the biogenic samples was indistinguishable from the background count rate at SQP(E) values below 570 [2].

For intercomparison purpose the following mixtures were used: commercial fossil fuels mixed with FAME – biogenic component produced from sunflower oil – with the reference biomass fractions of 20 %, 30 %, 40 %, 50 %,

60 %, 70 %, 80 % and 90 %, and FAME produced from lard fat with the reference biomass fractions 20 %, 30 % and 50 %.

RESULTS

The obtained results of intercomparison are presented in Table 1 and plotted in Figure 1. The results obtained at RBI for samples that were used for calibration at UNS are also presented.

Table 1. Biogenic fraction of various mixtures with referent biomass fraction determined by the two methods of data evaluation at UNS and RBI.

Referent biomass fraction (%)	**UNS biogenic fraction** (%)	**RBI biogenic fraction** (%)	**RBI SQP(E)** (channel)
Biogenic component – sunflower oil			
1	- *	1.6 ± 0.4	694
3	- *	10.8 ± 1.5	603
5	- *	-**	510
20	25.8 ±1.3	45.2 ± 1.5	622
30	39.0 ± 1.9	35.2 ± 0.7	724
40	49.9 ± 1.7	63.8 + 1.3	667
50	51.7 ± 2.0	44.9 ± 0.7	731
60	60.4 ± 2.2	81.5 ± 1.3	678
70	78.1 ± 2.7	75.6 ± 1.0	736
80	81.4 ± 2.9	89.8 ± 0.9	754
90	85 ± 3	91.7 ± 0.7	785
Biogenic component – lard fat			
3 winter	- *	3.5 ± 0.4	786
5 winter	- *	6.3 ± 0.4	788
7 winter	- *	7.7 ± 0.4	789
7 summer	- *	10.9 ± 0.5	713
10 summer	- *	13.0 ± 0.5	720
20	20.7 ± 0.7	-**	600
30	33.4 ± 1.9	-**	549
50	55.8 ± 1.1	-**	553

* used for calibration

** for SQP < 600, count rate of purely biogenic liquids is not distinguishable from the count rate of fossil liquids

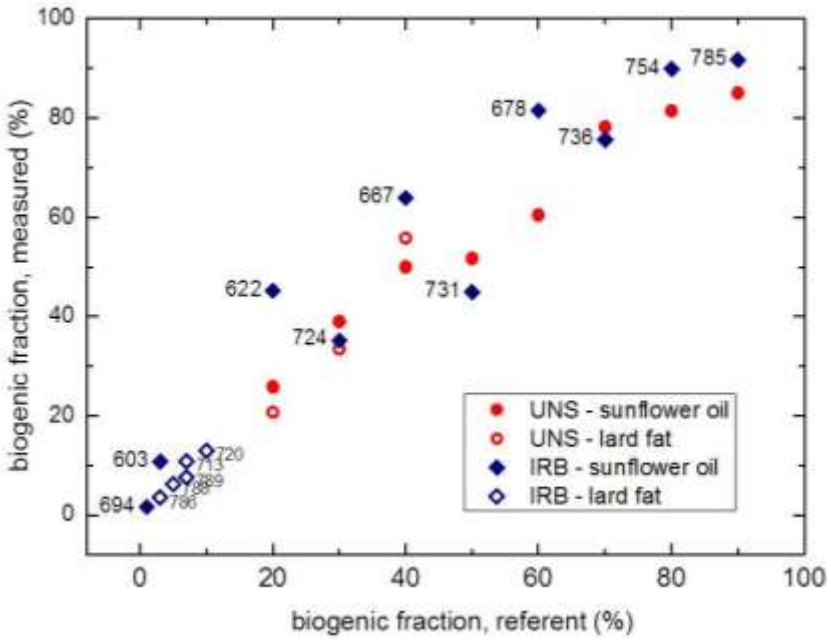

Figure 1. Correlation between the biogenic fraction measured at RBI and UNS and the referent biogenic fraction. The numbers represent the SQP(E) values of the corresponding samples measured at RBI.

By the presented comparison of the obtained results at RBI with the real biogenic component, the limitations of the RBI evaluation technique have been elucidated. The limit when the count rates of the biogenic and the fossil samples become indistinguishable has been moved from SQP(E) < 570 [2] to SQP(E)< 600. Moreover, large discrepancies were obtained for the SQP(E) values between 600 and 690 – the lower the SQP(E), the larger the relative differences between the measured and the expected biogenic fraction. The biogenic fraction can be successfully determined at SQP(E) > 690.

On the other hand, UNS had slight advantage in this intercomparison as they used the samples with the same matrices for calibration purposes. Two-step calibration procedure that UNS used implements quench correction and therefore offers more reliable ^{14}C determination in fuels in comparison to one-step calibration method [1]. The limitation of this method is that application of these calibration curves is limited to samples with chemically identical bio and fossil components. It can be used for precise biogenic fraction determination in examined fuel samples if the components of the fuel mixture are well known in advance.

CONCLUSION

RBI data evaluation method is based on two calibration curves, for purely biogenic and purely fossil liquids, and the calibration does not depend on the exact chemical composition of the organic liquid. The limits of the method are defined by the SQP(E) of approximately 690. Below this value the count rates of biogenic and fossil liquids become close to each other or even indistinguishable from one another.

UNS data evaluation method is very dependent on the composition of the examined fuels, so the obtained results were relatively good in this case. Future investigation should also test whether this calibration method is suitable for some other fuel matrices, for example for various types of domestic oils (vegetable, sunflower, olive, pumpkin, flax, peanut, corn sprouts) used in everyday life. This will be the next stage of this joint intercomparison in testing advantages and limitations of the RBI and UNS methods.

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REFERENCES

[1] Stojković I, Nikolov J, Tomić M, Mićić M, Todorović N. Biogenic fraction determination in fuels – Optimal parameters survey. Fuel 2017;191:330-338.

[2] Krajcar Bronić I, Barešić J, Horvatinčić N, Sironić A. Determination of biogenic component in liquid fuels by the ^{14}C direct LSC method by using quenching properties of modern liquids for calibration. Radiation Physics and Chemistry (2016) in press. Available on-line at http://dx.doi.org/10.1016/j.radphyschem.2016.01.041

[3] Krajcar Bronić I, Barešić J, Horvatinčić N, Krištof R, Kožar-Logar J. Nova tehnika određivanja udjela biogene komponente u tekućim gorivima metodom ^{14}C. U: Petrinec B, Bituh T, Milić M, Kopjar N, ur. Zbornik radova Desetog simpozija Hrvatskog društva za zaštitu od zračenja; 15-17. travnja 2015; Zagreb, Hrvatska. Zagreb: HDZZ; 2015. str. 360-365.

[4] Krištof R. Quantification of biocomponents in fuels by ^{14}C, dissertation, University of Nova Gorica Graduate School, Nova Gorica, 2015.

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European Union's promotion of the use of sustainable and renewable resources requires use of at least 10 % of synthesized biodiesel in liquid fuels by the year 2020. This legislation has stimulated various types of petrodiesel and bio-based component blends production, and development of methods for exact, effective and reliable quantification of biodiesel content. The method for determination of the biogenic fraction in liquid fuels by direct measurement of the ^{14}C activity concentration via liquid scintillation counting (LSC) technique was developed in few laboratories worldwide. It is based on different ^{14}C signatures of the two components: the biogenic component reflects the modern atmospheric ^{14}C activity, while no ^{14}C is present in fossil fuels. The quantity of ^{14}C in the fuel is the criterion for bio-fuel presence.

A great variety of biogenic matrices in fuels results in a wide range of quenching properties of different fuel mixtures. The laboratories participating in this intercomparison study developed two different calibration techniques. The Ruđer Bošković Institute data evaluation method is based on calibration curves for purely biogenic and purely fossil liquids, and does not depend on the exact chemical composition of the organic liquid. The limits of the method are defined by the SQP of app. 690 below which the count rate of biogenic and fossil liquids become indistinguishable from one another. The University of Novi Sad data evaluation method is very dependent on the composition of the examined fuels, so the obtained results in this case were relatively good. Future investigation should also test whether this calibration method is suitable for some other fuel matrices, for example for various types of domestic oil used in everyday life. Testing advantages and limitations of the two methods will continue in the future.