Determination of biogenic component in liquid fuels by the ^{14}C method and direct LSC measurement

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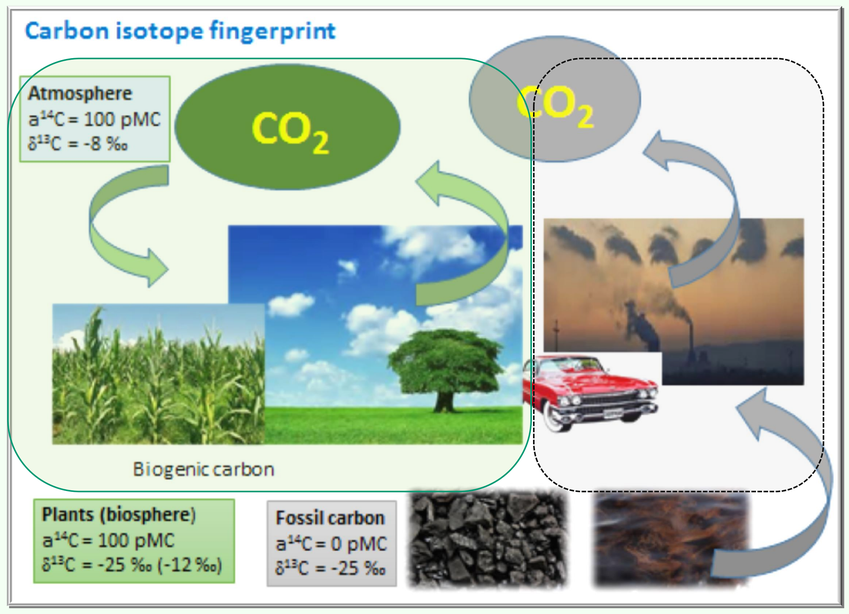
INTRODUCTION

Increase of CO_2 concentration in the atmosphere during the 20th century is a consequence of intensive use of fossil fuels. This effect can be slowed down by the use of biogenic materials for energy production and/or transport in addition to the use of renewable energy sources. The "environmentally kind politics" of the European Union stimulates the use of biogenic fuels by lower excise and income tax relief. Consequently, there is a need for independent determination of the fraction of the biogenic component in various types of fuels by reliable and accurate methods.

Biogenic materials itself or as blends to fossil fuels are presently often used for energy production and/or transport. One of the methods for determination of the fraction of the biogenic component in any type of fuel is the ^{14}C method.

biogenic – produced in natural processes by living organisms but not fossilized or derived from fossil resources
Fossil matrix: either gasoline (benzine) or diesel (gas oil)

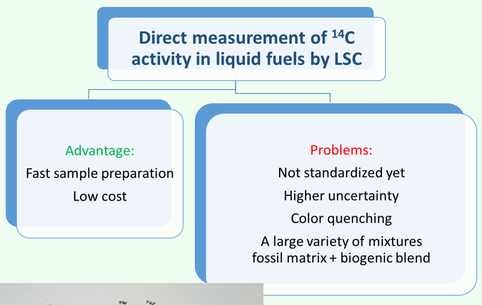


Carbon isotope characteristics ($\delta^{13}C$ and $a^{14}C$) of biogenic carbon, atmospheric CO_2 and fossil carbon. The use of fossil fuels causes introduction of excess CO_2 to the atmosphere.

^{14}C method for biogenic fraction determination

^{14}C method is based on different content of ^{14}C in biogenic (reflects the modern atmospheric ^{14}C activity) and in fossil component (no ^{14}C present). The ^{14}C method can be applied to various types of materials, such as solid communal waste, used car tyres, liquid fuels, consumable products, or CO_2 produced by combustion of various fuels.

A technique of direct LSC measurement of the ^{14}C content in liquid fuels is simple and fast because it does not require any sample pre-treatment. However, its main disadvantage is caused by different liquid colours that change quenching properties and measurement efficiency.



Liquids of different colours have different quenching properties and measurement efficiencies.

A material can be composed of a biogenic fraction (f_{bio}) and a fossil fraction (f_f): $f_f + f_{bio} = 1$

The measured ^{14}C activity of such a mixed material, $a^{14}C_{mix}$, is a combination of the biogenic and fossil components:

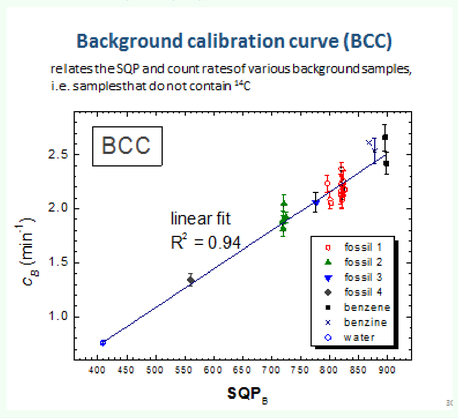
$$a^{14}C_{mix} = f_f\, a^{14}C_f + f_{bio}\, a^{14}C_{bio}$$

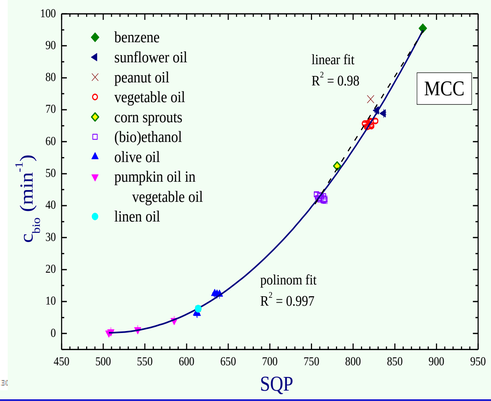
In fossil fuels all ^{14}C had been decayed, $a^{14}C_f = 0$ pMC, → the fraction of the biogenic component can be determined as

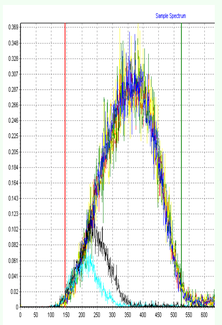
$$f_{bio} = a^{14}C_{mix} / a^{14}C_{bio}$$

We proposed [1] a new evaluation technique that takes advantage of different quenching properties of various liquids of different colours. Various modern organic liquids (various brands of domestic oils, benzene, bioethanol) were used to construct the modern calibration curve (MCC) that relates their count rates and SQP (standard quench parameter) values. A background calibration curve (BCC) was constructed by using various ^{14}C-free liquids. We suggested that the data evaluation method could be used for determining the biogenic fraction in various types of organic liquids, including liquid fuels of unknown chemical composition.

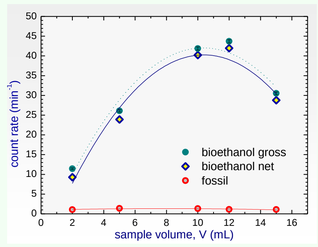
[1] Krajcar Bronić, I, et al. **Determination of biogenic component in liquid fuels by the 14C direct LSC method by using quenching properties of modern liquids for calibration**. *Radiation physics and chemistry (1993)*. (2016) doi: 10.1016/j.radphyschem.2016.01.041







Determination of the best sample to UGF cocktail ratio, spectra recorded by LSC Quantulus, window 124 – 570 channels, low-potassium glass vials of 20 ml

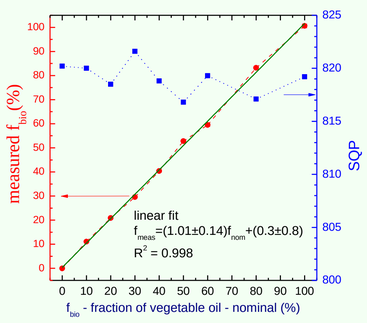


The fraction of the biogenic component in the sample is calculated as the ratio of net count rates of the sample to the biogenic material.

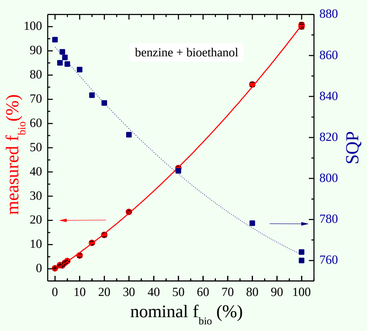
$$f_{bio} = (c - c_B) / (c_{bio} - c_B)$$

We prepared mixtures of ^{14}C-free and biogenic liquids in a nominal concentration range of the biogenic component from 0 % to 100 %. We used liquids with different SQP values

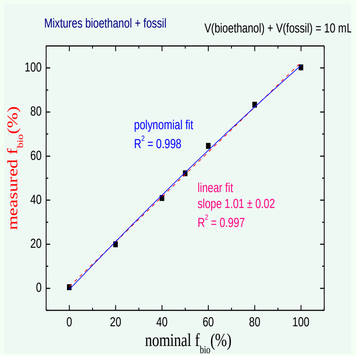
Mixture of a biogenic and a fossil liquid with similar SQP

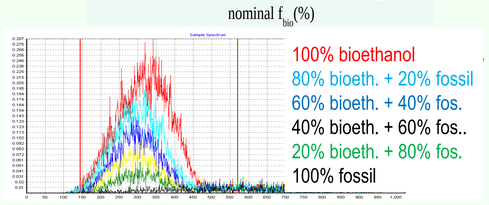


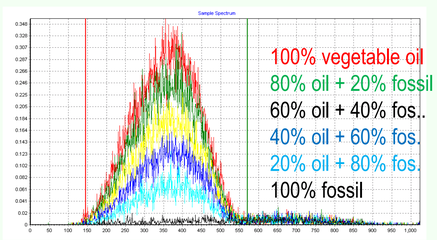
Mixture of biethanol and analytically pure benzine



Mixture of bioethanol and a fossil liquid, different SQP







Intercomparisons of the new data evaluation techniques with the „standard" evaluation technique:
Krajcar Bronić I., J. Barešić, N. Horvatinčić, R. Krištof , J. Kožar-Logar: New technique of determination of biogenic fraction in liquid fuels by the ^{14}C method. Proc. 10th Symp. of Croatian Radiation Protection Association, pp. 390-395, Šibenik, Croatia, 2015.
Nikolov J., I. Krajcar Bronić, I. Stojković, N. Todorović, J. Barešić, M. Krmpotić, M. Tomić: Comparison of two different methods for determination of biogenic fraction in liquid fuels. Proc. 11th Symp. of CRPA, pp. 206-211, Osijek, Croatia, 2017.

CONCLUSION

Determination of the biogenic fraction in various materials is an interesting topic for the scientists, for various industries and for the global environment. The ^{14}C method is a very powerful method for determination of the biogenic fraction in any material. A direct measurement method in LSC can be used for liquid fuels.

The proposed data evaluation technique of the direct measurement of ^{14}C activity of liquid fuels in LSC depends neither on the fossil matrix or the biogenic additive type, it does not require ^{14}C spikes or other expensive standards. One does not need to know the qualitative composition of the fuels, as it is the case for other evaluation techniques. Mixtures of a biogenic and a ^{14}C-free liquids demonstrated the potential of the proposed technique for determining the biogenic fraction of a mixture. The limit when the count rates of the biogenic and the fossil samples become indistinguishable is set to SQP ≈ 600. The method gives comparable results with other data evaluation techniques, and the results are very good for SQP > 700.