NEW DEVELOPMENTS IN THE DIRECT LSC METHOD OF BIOGENIC COMPONENT DETERMINATION IN LIQUID FUELS BY ^{14}C

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Radiocarbon (^{14}C) method is a very powerful method for fast and accurate determination of bio-based fraction in any material containing carbon. Any radiocarbon measurement technique can be applied; however, for liquid fuels the best technique is a direct measurement of liquids mixed with a scintillation cocktail in liquid scintillation counters – the direct LSC technique.

At the first conference Natural Resorces, Greeen Technology & Sustainable Development in 2014 we presented a new data evaluation technique for determination of biogenic fraction in liquid fuel by the ^{14}C direct LSC method. The idea was to use various purely biogenic compounds of different colours and quenching properties to construct the “modern calibration curve”, as well as various purely fossil liquids to construct the “background calibration curve”. The fraction of the biogenic component in an unknown sample was determined as the ratio of net count rates of the unknown sample and the biogenic sample having the same quenching properties. The proposed data evaluation technique depended neither on the fossil matrix nor on the biogenic additive type. It did not require ^{14}C spikes or other expensive standards. One did not need to know the qualitative composition of liquid fuels, as it was the case for other evaluation techniques. Mixtures of biogenic and ^{14}C-free liquids demonstrated the potential of the proposed technique for determining the biogenic fraction of a mixture.

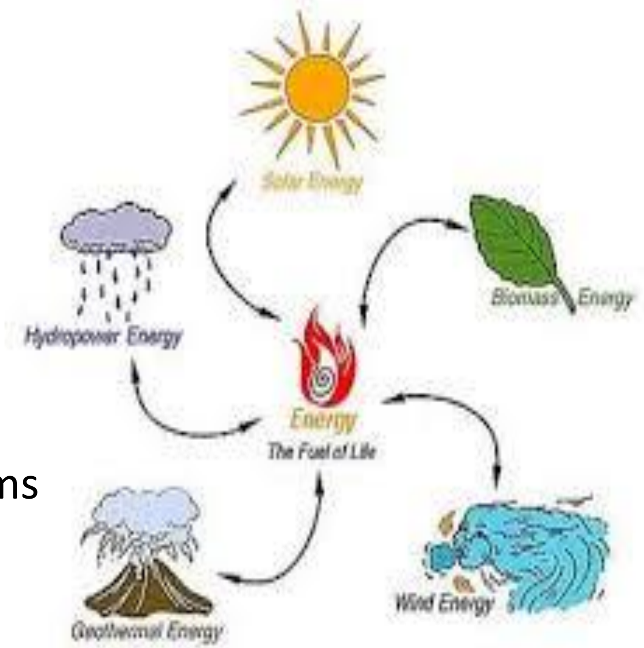
In this presentation we would like to report developments in the direct LSC technique, results of intercomparison studies with other laboratories that apply a conventional evaluation technique, as well as results of determination of the biogenic component fraction in mixtures of various fossil matrices and various biogenic blends. The limit when the count rates of the biogenic and the fossil samples become close to each other or indistinguishable is set to SQP ≈ 700, where SQP denotes the Standard Quench Parameter determined by LSC Quantulus 1220. Below this value the obtained results for biogenic fractions are not reliable. The method gives comparable results with other data evaluation techniques, and the results are very good for SQP > 700. Influence of aging of both original mixtures and prepared scintillation cocktails on SQP and count rate will be discussed.

Intensive use of fossil fuels for energy production and transport during 20th century caused an increase of CO_2 concentration in the atmosphere.

How do we know that excess-CO_2 comes from fossil fuels?

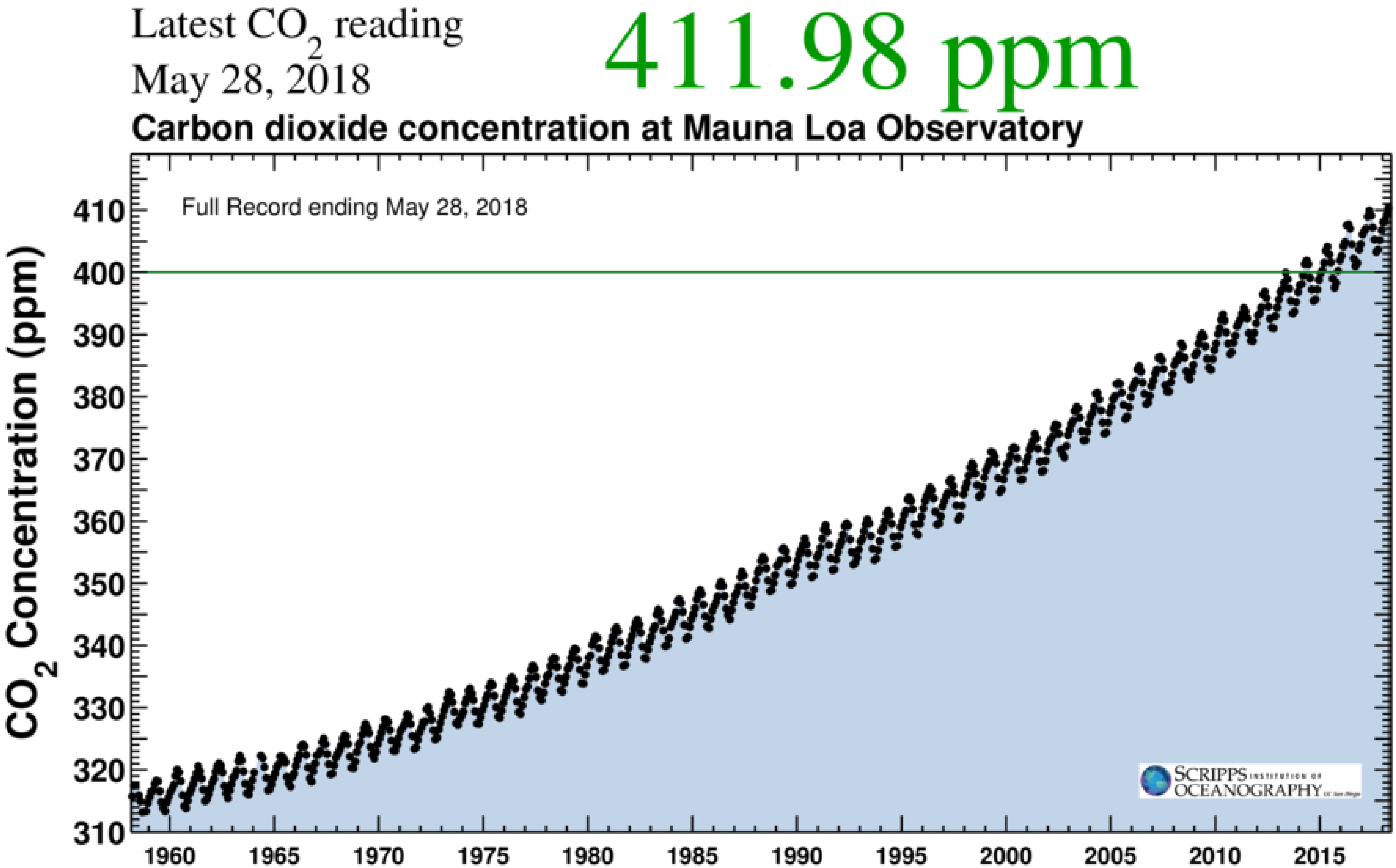
What to do to stop or at least slow-down the increase of atmospheric CO_2 concentration?

The increase of CO_2 concentration can be slowed down by the use of renewable energy sources - biogenic materials for energy production and/or transport



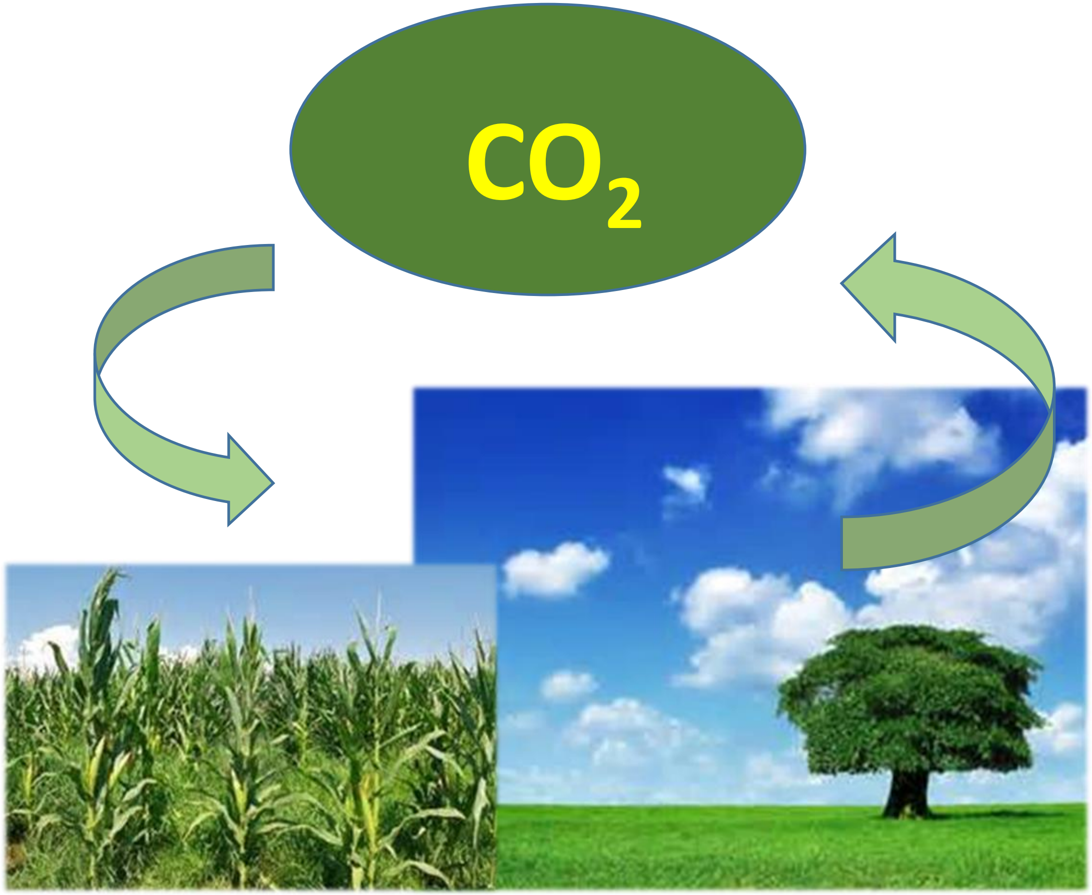
biogenic – produced in natural processes by living organisms but not fossilized or derived from fossil resources

How can we determine the biogenic fraction in any type of fuel?
The ^{14}C method, which is based on different content of ^{14}C in biogenic and in fossil component, is a reliable method and can be used for various types of fuels.



https://scripps.ucsd.edu/programs/keelingcurve/wp-content/plugins/sio-bluemoon/graphs/mlo_full_record.png

Carbon cycle



Biogenic carbon

All carbon isotopes take part

^{12}C

^{13}C

^{14}C

Carbon on Earth

^{12}C: 98.89 %

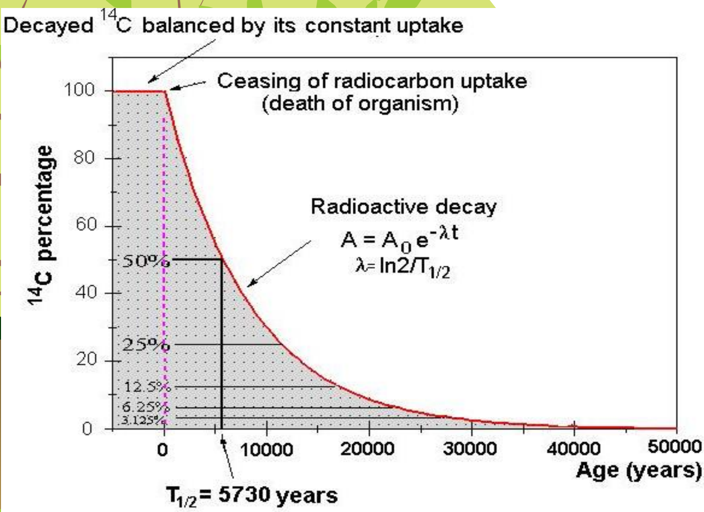
^{13}C: 1.1 %

^{14}C: 1.18 x 10^{-10} %

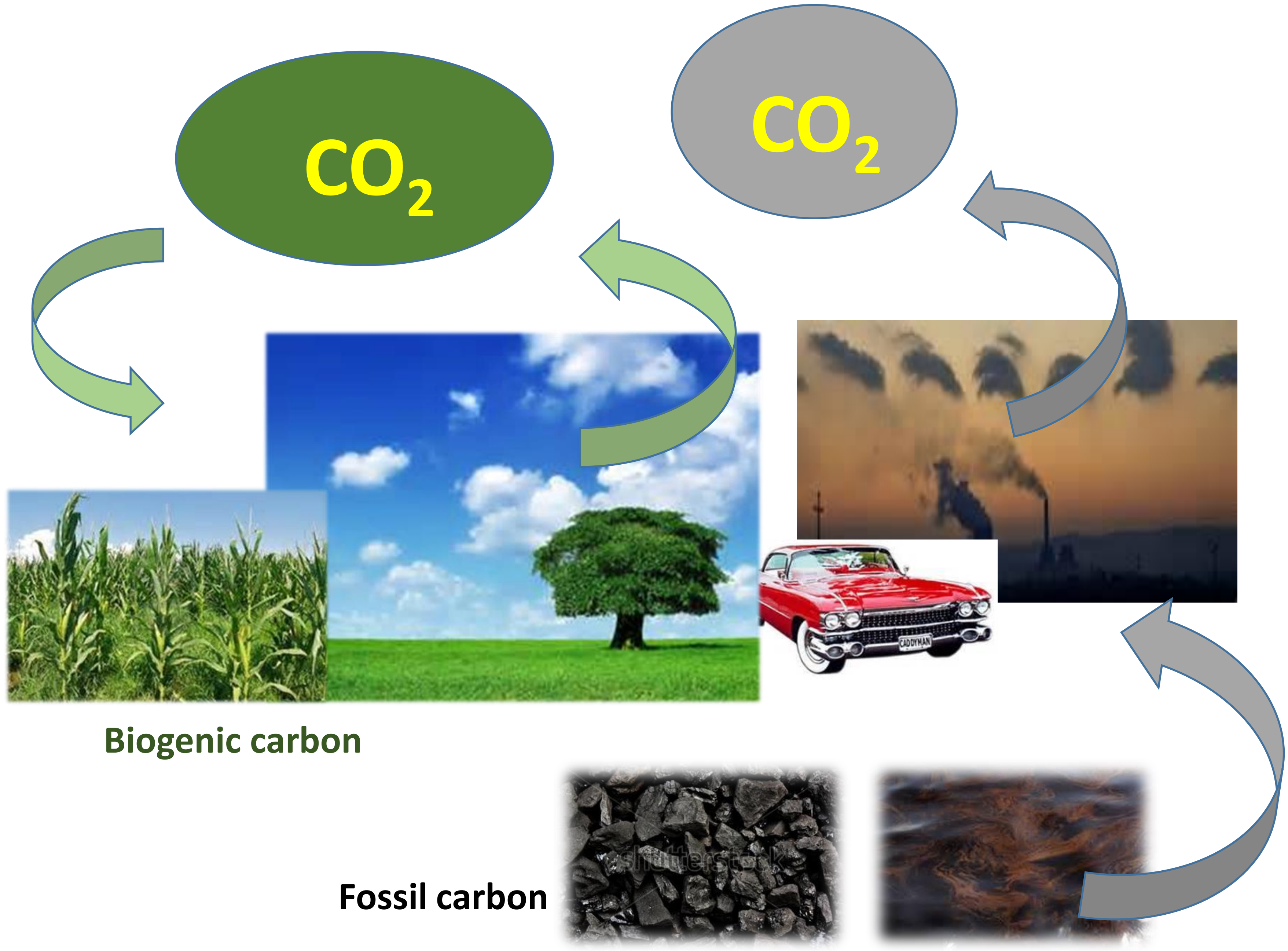
$$^{14}N + n \rightarrow {}^{14}C + p$$

O_2

$^{14}CO_2$



$$^{14}C \rightarrow {}^{14}N + e + \overline{\nu}$$



CO2
CO2
Biogenic carbon
Fossil carbon

Carbon isotope fingerprint

Atmosphere
$a^{14}C$ = 100 pMC
$\delta^{13}C$ = -8 ‰

CO_2

CO_2

Biogenic carbon

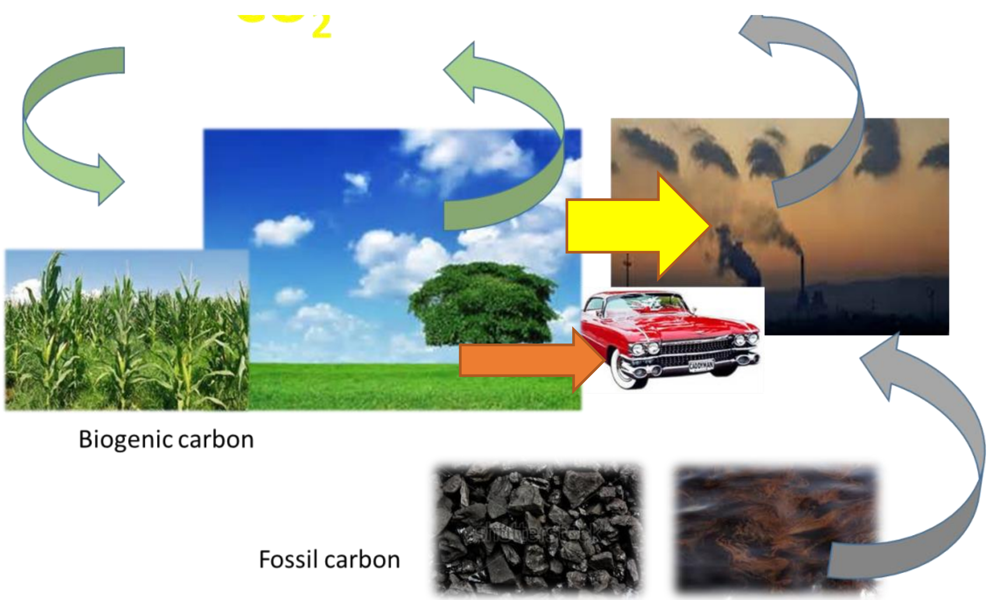
Plants (biosphere)
$a^{14}C$ = 100 pMC
$\delta^{13}C$ = -25 ‰ (-12 ‰)

Fossil carbon
$a^{14}C$ = 0 pMC
$\delta^{13}C$ = -25 ‰

From the presented data we can conclude

- Intensive use of fossil fuels for energy production and transport during 20th century caused an increase of CO_2 concentration in the atmosphere

What to do to stop or at least slow-down the increase of atmospheric CO_2 concentration?



The increase of CO_2 concentration can be slowed down by the use of biogenic materials for energy production and/or transport.

Production of biofuel is more expensive than the use of fossil fuel

The "environmentally kind politics" of the European Union stimulates the use of biogenic fuels by lower excise and income tax relief.

Countries throughout the world have set new targets for the minimum content of biogenic materials in fuel (5.75% until 2010 in Europe, 2003/30/EC; EU Directive 2009/28/EC at least 10 % of bio-fuel in all (liquid) fuels by 2020).

Thus, there is a **need for independent determination of the fraction of the biogenic component in various types of fuels by reliable and accurate methods.**

Methods for determination of fraction of biogenic component in any type of fuel or waste used in waste-to-energy plants

1 - manual sorting

2 - chemical dissolution

3 - ^{14}C method

ASTM D6866-12 Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis. ASTM International. 2012.

^{14}C method is based on different content of ^{14}C in biogenic and in fossil component: while the biogenic component reflects the modern atmospheric ^{14}C activity, no ^{14}C is present in fossil fuels.

^{14}C method is suitable for samples of all types of fuel

"Problems" or limitations: i) the measurement of ^{14}C content requires highly specialized instruments and personnel (this standard gives a number of about 100 radiometric and 40 AMS laboratories on the global scale!),
ii) ^{14}C releases in the 1950's ("bomb-peak") has diminished the accuracy of the ^{14}C method in some cases

A pure biogenic material reflects the modern atmospheric ^{14}C activity, while no ^{14}C is present in fossil fuels (oil, coal). Therefore, a biogenic fraction of any material of interest is proportional to its ^{14}C content .

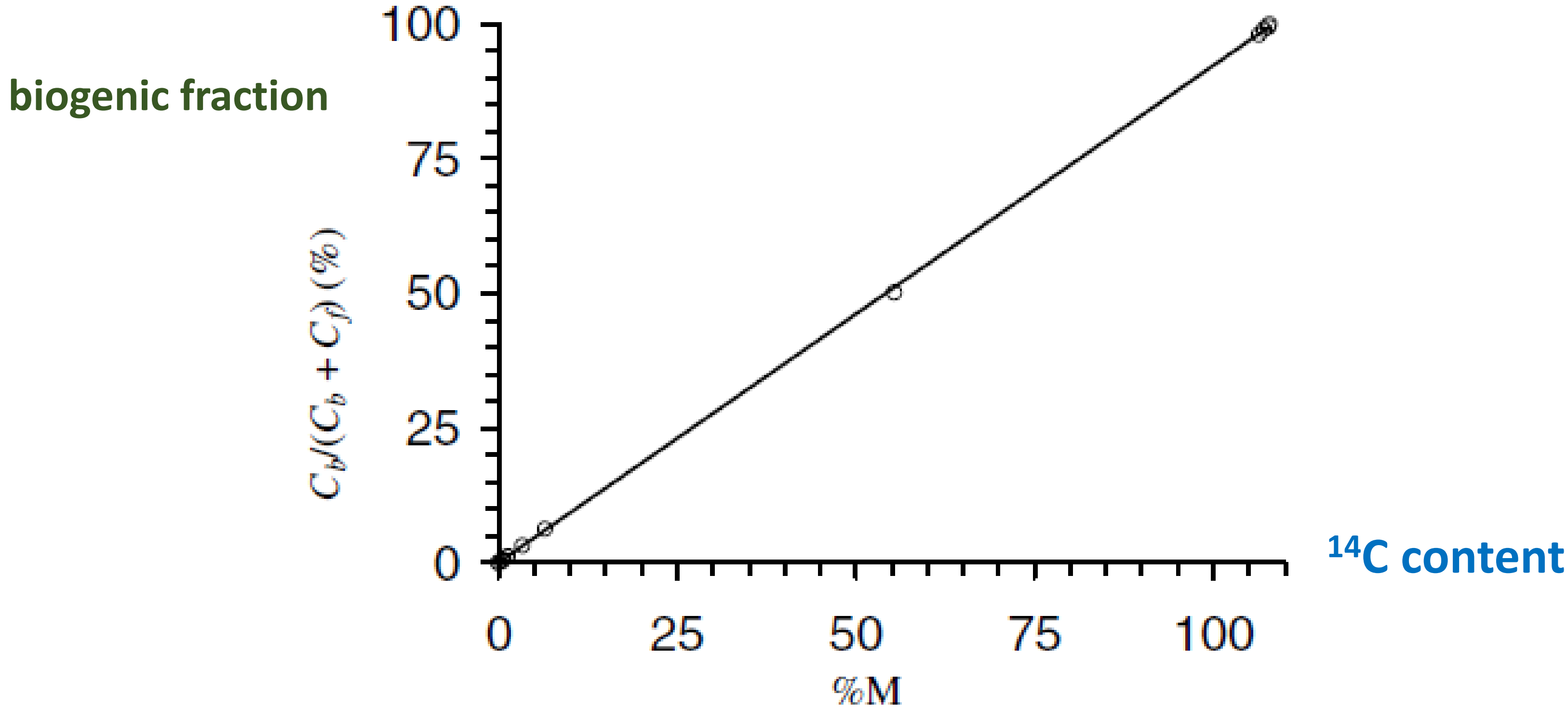


Figure 2 Biofuel carbon : total carbon ratio in the fuel sample ($C_b/(C_b + C_f)$) versus percent Modern (%M) by ^{14}C LSC, 5.5 hr counting; linear fit: $C_b/(C_b + C_f) = 0.9231 \times \%M$, $R^2 = 0.9999$.

RADIOCARBON, Vol 48, Nr 3, 2006, p 315–323

QUANTITATIVE DETERMINATION BY ^{14}C ANALYSIS OF THE BIOLOGICAL COMPONENT IN FUELS

Ivo J Dijs[1,2] • Eric van der Windt[1] • Lauri Kaihola[3] • Klaas van der Borg[4]

The ^{14}C method is the most reliable method of determination of the biogenic fraction in fuels. It can be applied to various types of fuels used, such as solid communal waste, used car tyres, liquid fuels.

It can be used also to determine the biobased content of **various manufactured products** (e.g., solvents and cleaners, lubricants, construction material, carpets…)

G.A. Norton and S.L. Devlin. Determining the modern carbon content of biobased products using radiocarbon analysis. *Bioresource Technology* 97 (2006) 2084–2090.

Alternatively, the ^{14}C method can be applied to determine **^{14}C content of the CO_2** produced by combustion of various fuels in waste-to-energy plants

J. Mohn, S. Szidat, J. Fellner, H. Rechberger, R. Quartier, B. Buchmann, L. Emmenegger. Determination of biogenic and fossil fuel CO_2 emitted by waste incineration based on $^{14}CO_2$ and mass balances. *Bioresource Technology* 99 (2008) 6471–6479

G.K.P Muir, S. Hayward, B.G. Tripney, G.T. Cook, P. Naysmith, B.M.J. Herbert, M.H. Garnet, M. Wilkinskon. Determining the biomass fraction of mixed waste fuels: A comparison of existing industry and ^{14}C-based methodologies. *Waste management* 35 (2015) 293-300.

How to determine biogenic fraction by the ^{14}C method

Results of measurement are presented as relative specific ^{14}C activity, $a^{14}C$, expressed in percent of modern carbon (pMC)
100 pMC = 226 Bq/kgC

A material can be composed of a biogenic component (of fraction f_{bio}) and a fossil component (f_f)

$$f_f + f_{bio} = 1$$

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

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

Since in fossil fuels all ^{14}C had been decayed, and $a^{14}C_f = 0$ pMC, it follows that the fraction of the biogenic component can be determined as

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

Comparison of characteristics (precision, complexity, and price) of various techniques for biogenic fraction determination by the ^{14}C method.

Measurement technique	Sample types	Required mass of carbon	Complexity *	Precision *	Price *	Main drawback
AMS	all	~1 mg	3	4	4	representativeness of the sample ##
LSC-benzene #	all	~4 g	4	3	3	time-consuming
LSC-CO_2 #	all	~0.6 g	2	2	2	high uncertainty low sensitivity
LSC-direct	liquid fuels	10 ml of liquid	1	1	1	quenching

* The higher the number, the more complex the method / the lower the uncertainty / the higher the price

\# Oxidation is critical because samples tend to explode (liquid fuels)
\## Sample heterogeneity: Advantageous to use gram size quantities and LSC

Liquid fuels

According to the EU Directive 2009/28/EC [14] all (liquid) fuels have to contain at least 10 % of bio-fuel, i.e., blend of biogenic origin, by 2020.

Fossil matrix of the fuels is either gasoline (benzine, petrol) or diesel (gas oil), while **biogenic blends** are usually bioethanol, fatty acid methyl esters (FAMEs), hydrogenated vegetable oil (HVO) and others.

Biofuels - definition

are liquid or gaseous fuels for transport produced from biomass.

Directive 2003/30/EC on the promotion of the use of biofuels or other renewable fuels for transport - at least the following products shall be considered as biofuels: bioethanol, biodiesel, biogas, biomethanol, biodimethylether, bio-ETBE (ethyl-tertio-butyl-ether), bio-MTBE (methyl-tertio-butyl-ether), synthetic biofuels, biohydrogen and pure vegetable oil.

Direct measurement of ^{14}C activity in liquid fuels by LSC

Advantage:

Fast sample preparation

Low cost

Problems:

Not standardized yet

Higher uncertainty

Color quenching

A large variety of mixtures
fossil matrix + biogenic blend

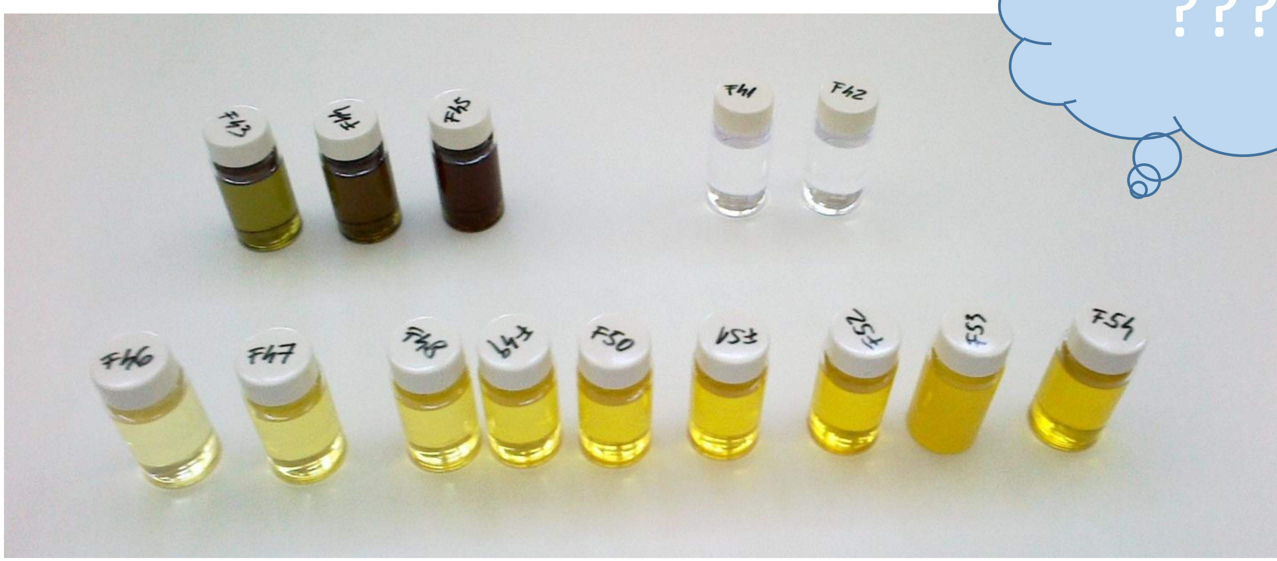
Various colors of fuels cause different counting properties (SQP - quenching, counting efficiency)

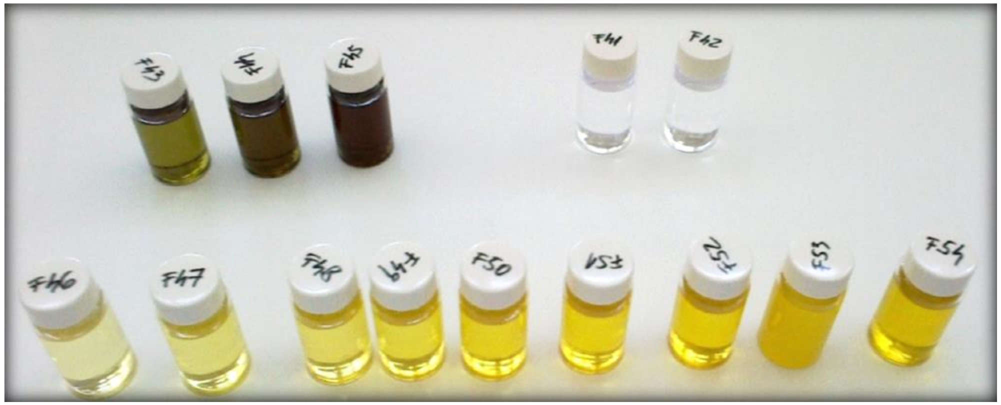
Various methods have been suggested to overcome this problem

- Different quenching curves for various combinations of the fossil matrix and biogenic blends by using ^{14}C spikes
- Various methods of decolorization - bleaching
- Different evaluation techniques of the LSC spectra for different combinations f.f. + b.b.

We were looking for a simple, fast, robust technique, though reliable and accurate, that would depend neither on the type of the fossil matrix nor on the type of the biogenic blend

???





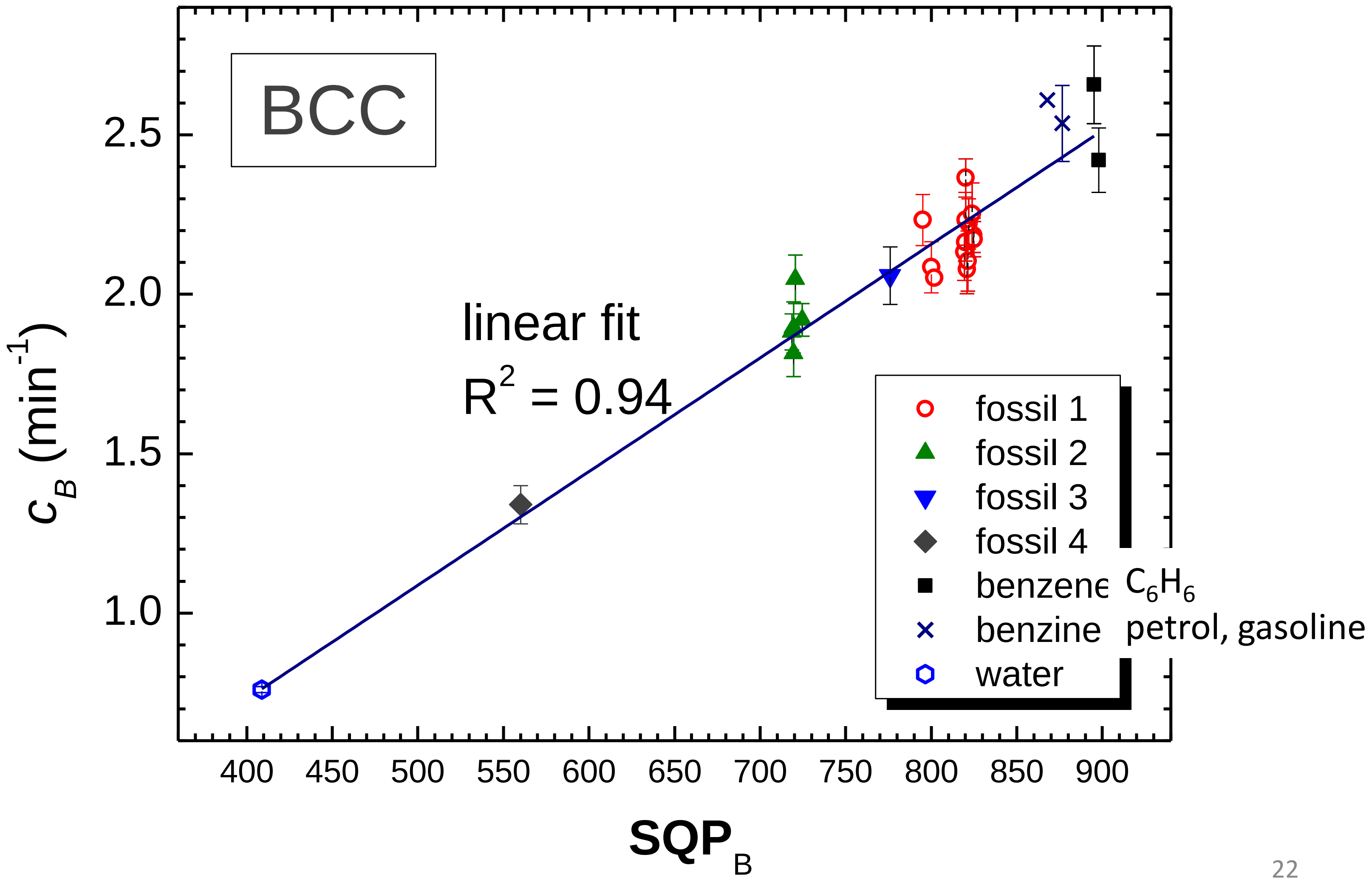
Idea!

Convert the problem/main drawback to the advantage - **quenching parameter of various samples use as the calibration parameter**!

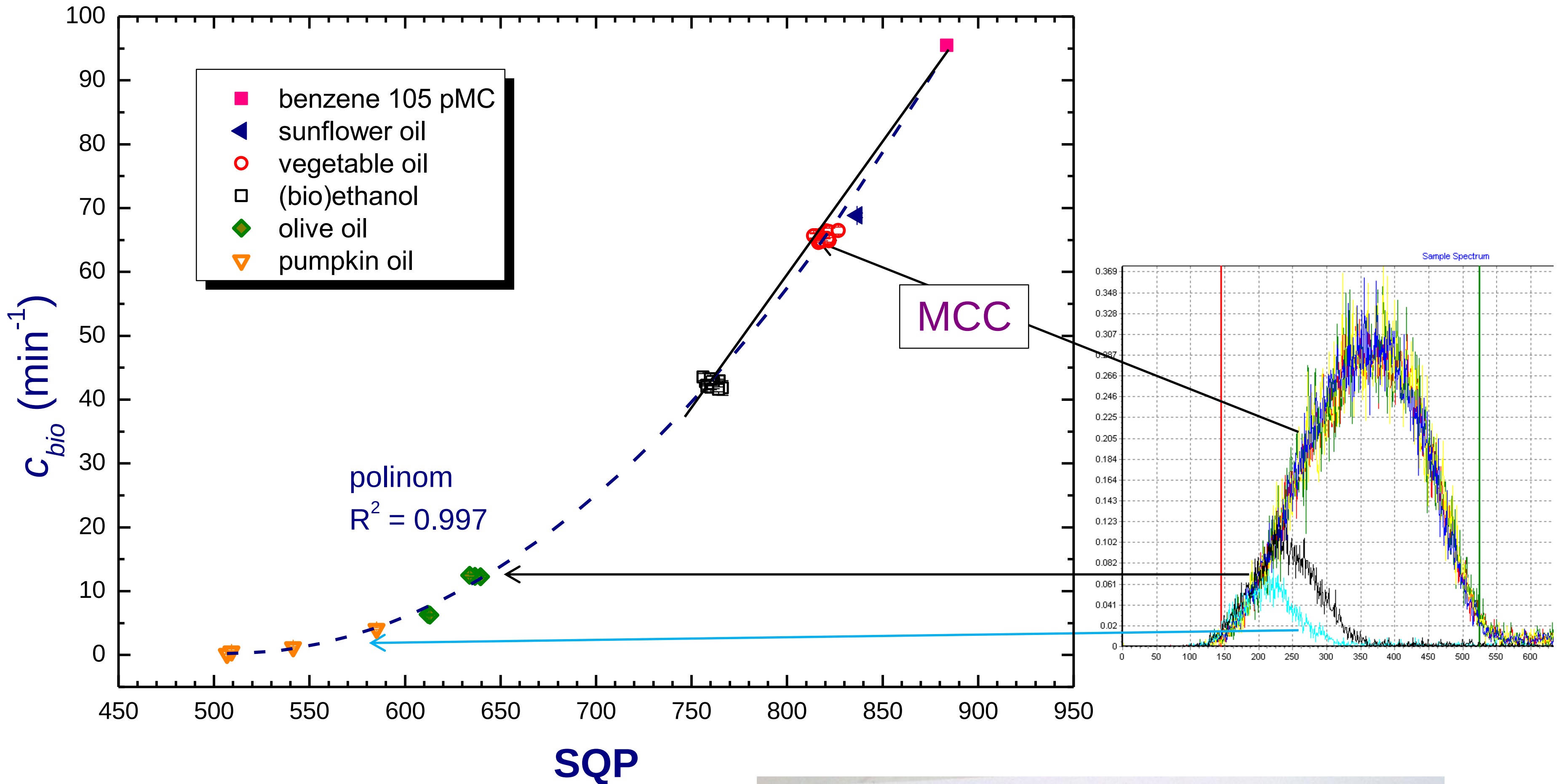
By using different 100% biogenic and 100% fossil liquids of different colors we determined a relation between the two quantities measured by LSC Quantulus: SQP parameter and count rate

Background calibration curve (BCC)

relates the SQP and count rates of various background samples, i.e. samples that do not contain ^{14}C



Modern calibration curve (MCC)



Liquid of biogenic origin: various brand of domestic oil, (bio)etanol p.a., benzene (modern samples)

The procedure of data evaluation for the unknown sample:

- measurement of SQP and count rate of the sample (SQP, c)
- determination of background count rate corresponding to the measured SQP value by using BCC (b)
- determination of the count rate of the biogenic sample (c_{bio}) corresponding to the measured SQP values by using MCC

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.

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

All samples should be measured under the same conditions:

- low-potassium glass vials of 20 ml
- scintillation cocktail UltimaGoldF (UGF)
- the ratio sample:UGF 10 ml : 10 ml
- spectra recorded by LSC Quantulus evaluated in the window 124 – 570 channels

The lowest detectable biogenic fraction is 0.5 % for measurement duration of 600 minutes

Test and validation

various mixtures of fossil and biogenic liquids in the nominal concentration ranges of the biogenic component from 0 % to 100 %.

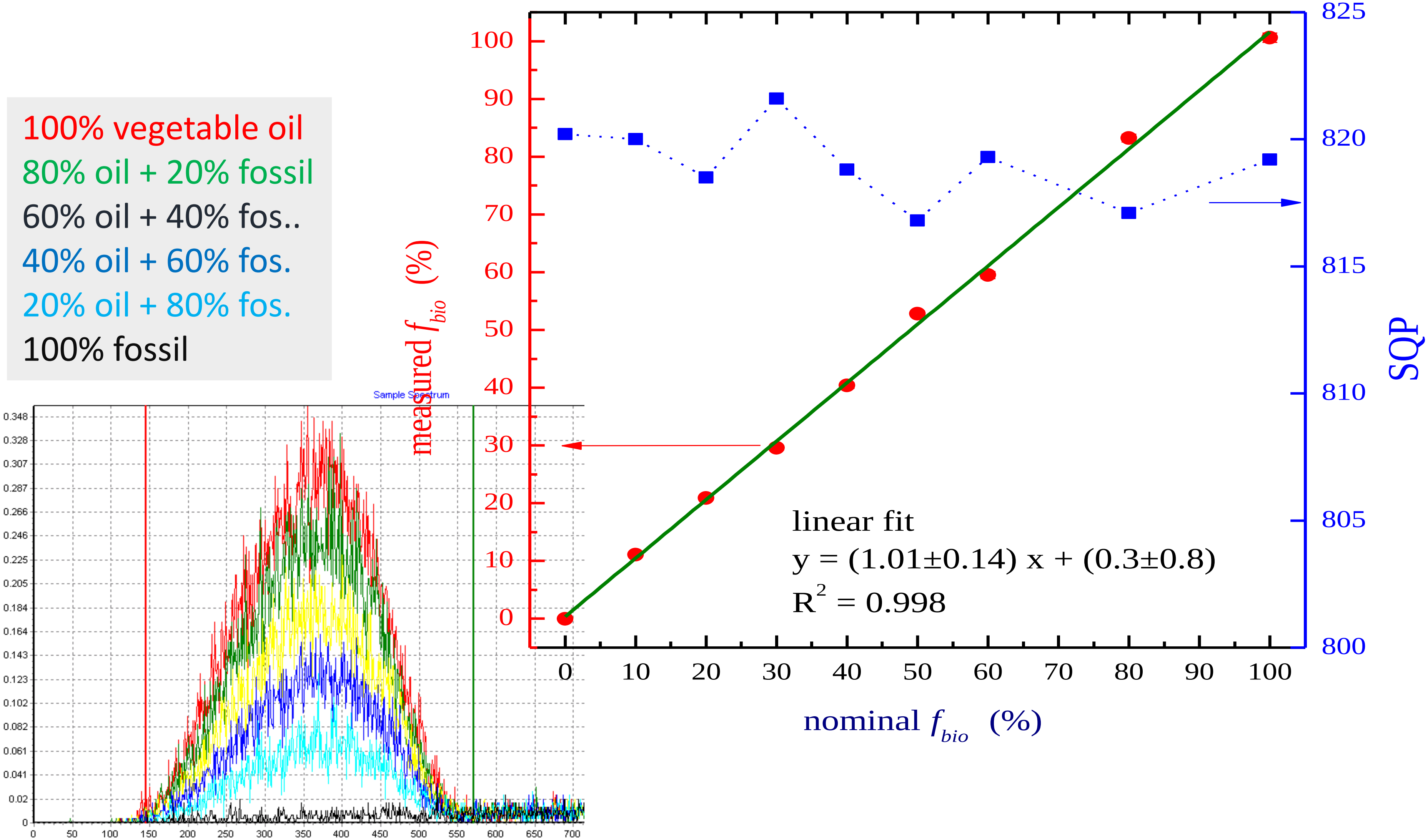
- vegetable oil and fossil fuel that both have approximately the same value of the SQP parameter
- bioethanol and fossil fuel with different SQP values
- bioethanol and ^{14}C-free benzine

In all cases, the calculated biogenic fraction agreed well with the nominal fraction.

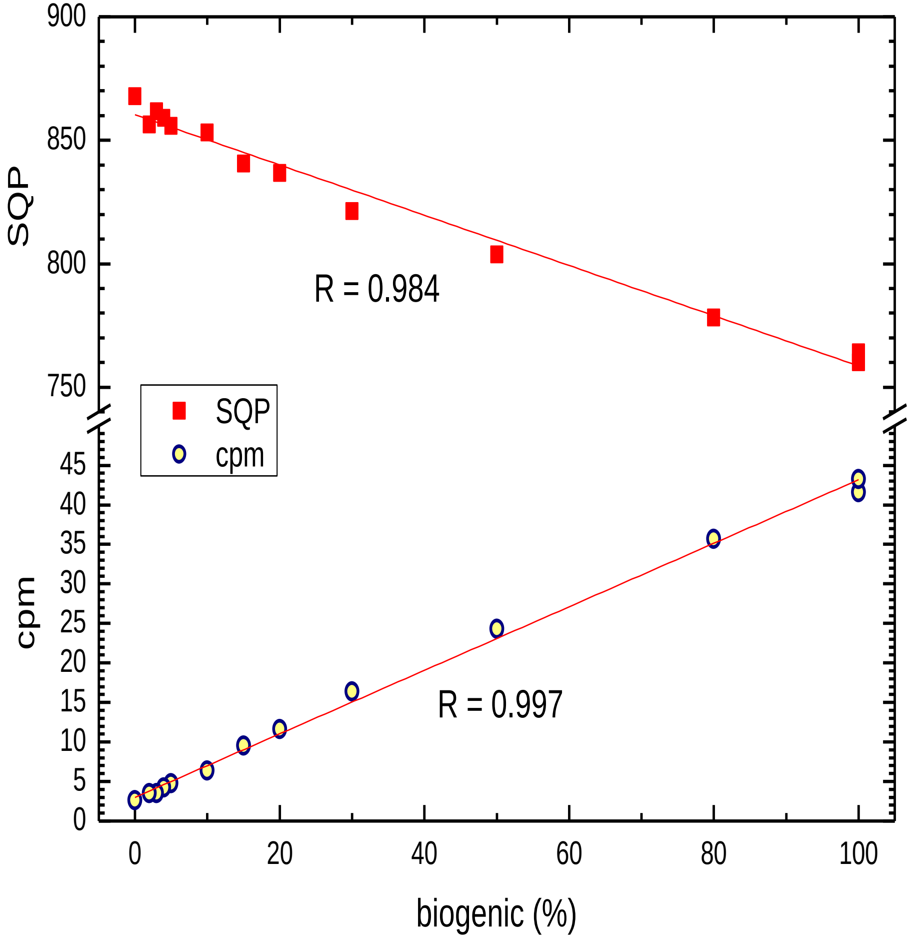
- mixtures of two different biogenic liquids (vegetable oil and bioethanol, vegetable oil and olive oil) having different SQP

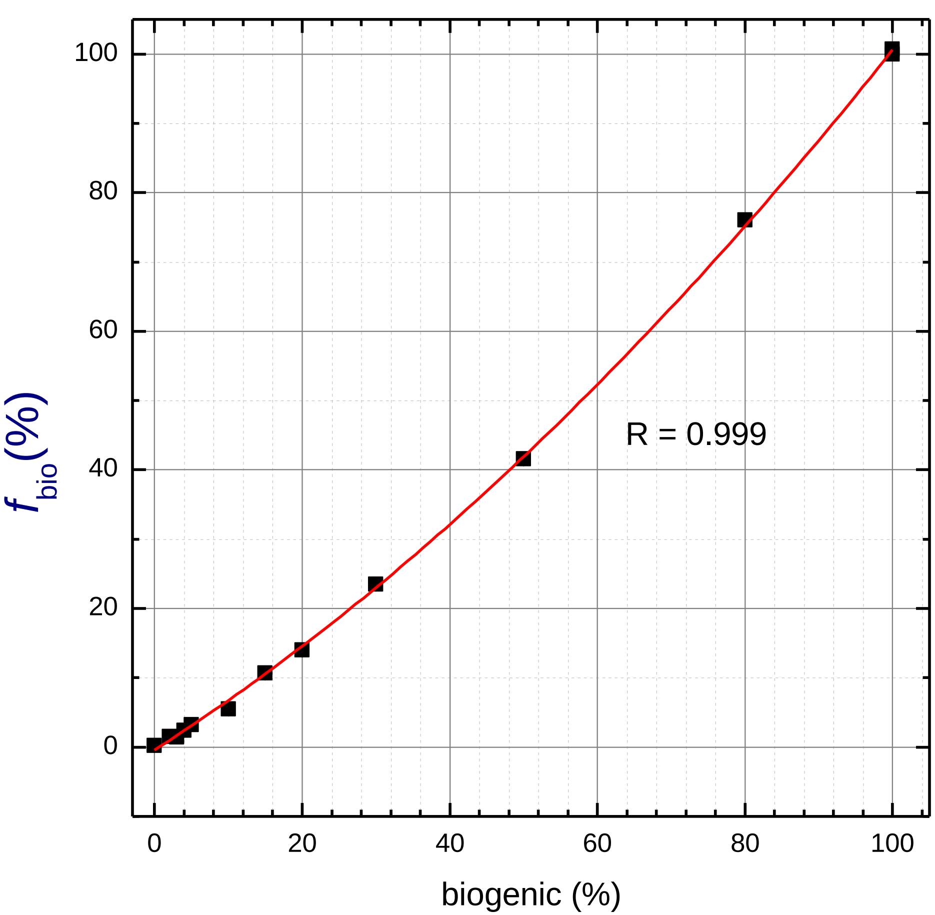
mixtures of vegetable oil and fossil fuel, similar SQP

The measured f_{bio} values agree very well with the nominal f_{bio} values while the SQP values of all mixtures remained more-or-less constant.

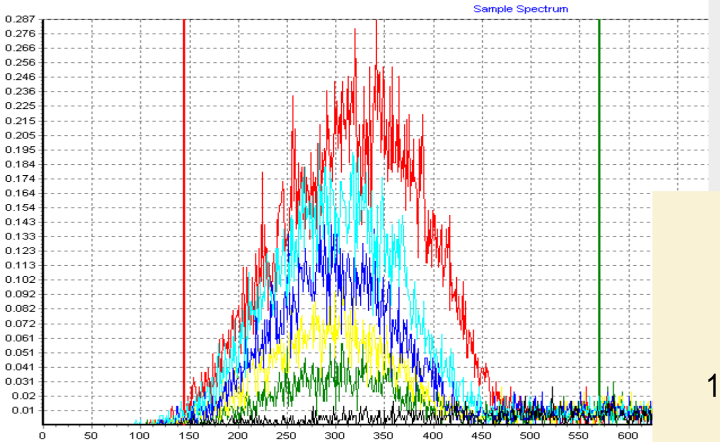


Bioethanol and benzine p.a. mixtures (different SQP)





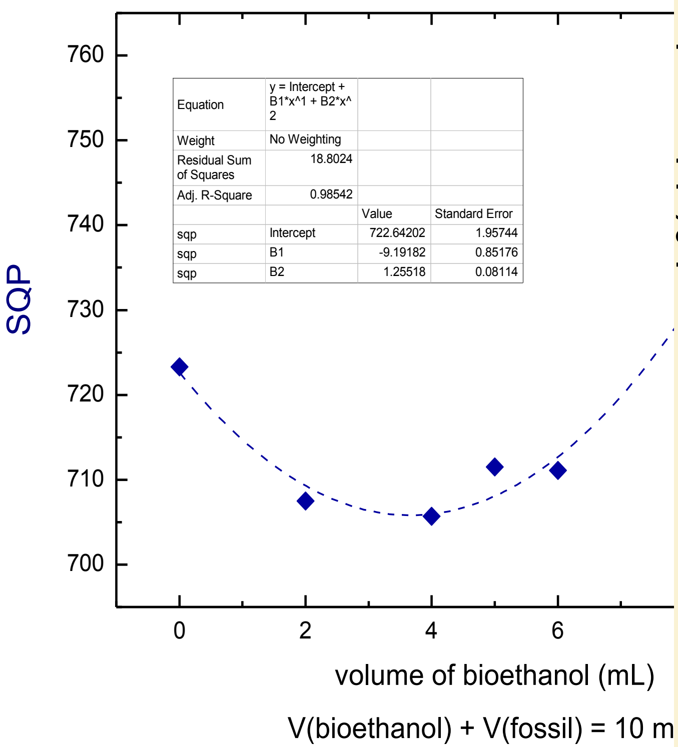
Bioethanol and fossil fuel mixtures of different SQP



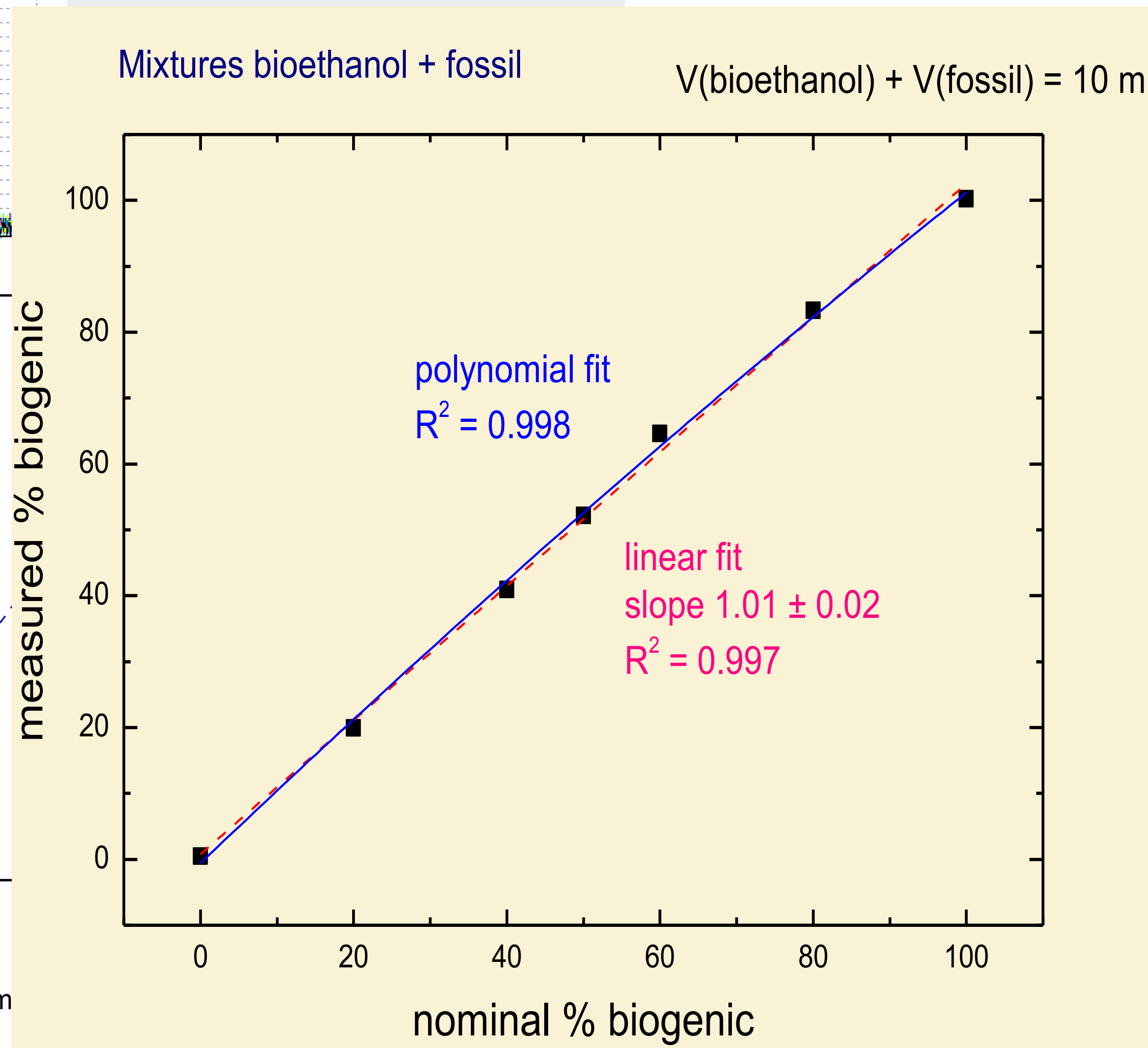
100% bioethanol

80% bioeth. + 20% fossil

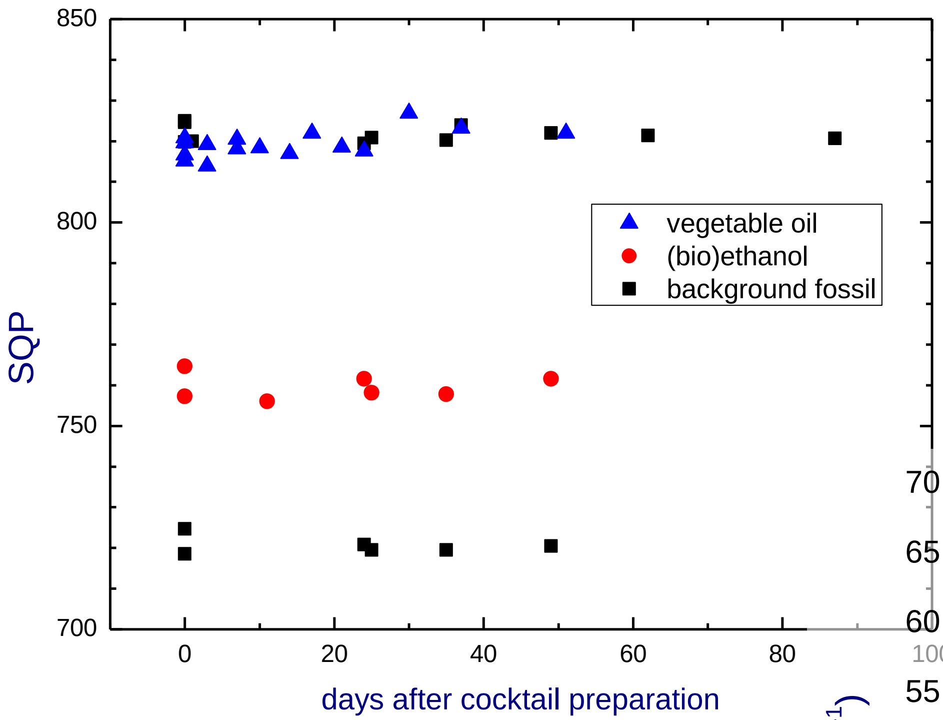
60% bioeth. + 40% fos.



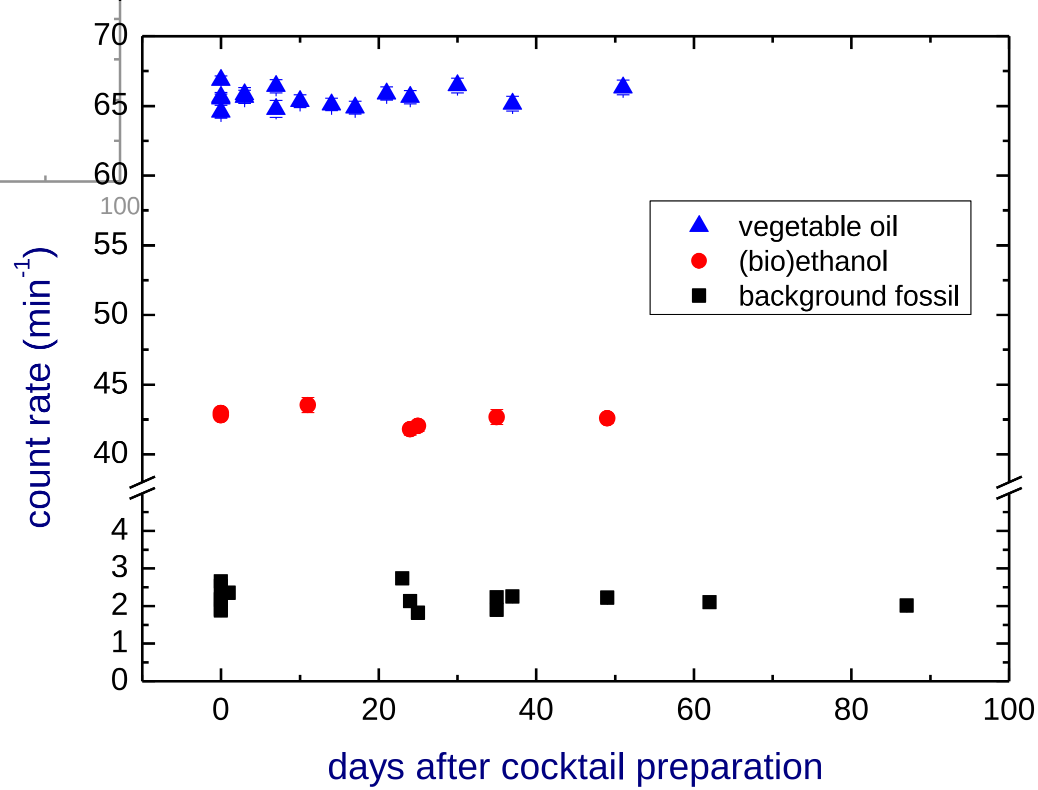
Equation	y = Intercept + B1*x^1 + B2*x^2		
Weight	No Weighting		
Residual Sum of Squares	18.8024		
Adj. R-Square	0.98542		
		Value	Standard Error
sqp	Intercept	722.64202	1.95744
sqp	B1	-9.19182	0.85176
sqp	B2	1.25518	0.08114



Long-term stability of SQP and count rate - aging



No change in either SQP or count rate was observed - the prepared cocktails are stable during at least 3 months after preparation.



Intercomparison

The obtained results were in good agreement with those obtained by different evaluation technique, both for the gasoline and diesel as the fossil matrix and various biogenic blends.

I. Krajcar Bronić, J. Barešić, N. Horvatinčić, R. Krištof and J. Kožar-Logar. New technique of determination of biogenic fraction in liquid fuels by the 14C method. Proc. 10th Symp. of Croatian Radiation Protection Association, pp. 390-395, Šibenik, Croatia, 15-17 April 2015. HDZZ, Zagreb, 2015

no.	Fuel matrix	RBI Zagreb		JSI Ljubljana	
		SQP	f_{bio} (%)	SQP	f_{bio} (%)
1	diesel	636.3	8.2 ± 0.8	657.3	7 (nominal)
2	diesel	716.9	2.2 ± 0.3	742.4	1.73 ± 0.10
3	diesel	758.3	5.8 ± 0.3	771.8	5.17 ± 0.26
4	diesel	885.8	0 (< 0.5)	880.3	0.5 ± 0.3 (< 0.52)
5	diesel	776.8	0.64 ± 0.30	776.2	0.62 ± 0.37
6	gasoline	841.6	0.1 ± 0.1 (< 0.5)	838.9	0.26 ± 0.19 (< 0.57)
7	gasoline	790.7	3.1 ± 0.2	790.6	5.22 ± 0.57
8	gasoline	823.4	3.4 ± 0.2	828.4	4.44 ± 0.43

Conclusion

Determination of the biogenic fraction in various materials is an interesting topic for the scientists, for various industries and for the global environment, because the use of biogenic materials for energy production and transport may slow down the increase of atmospheric CO_2 concentration of fossil origin.

The ^{14}C method is a very powerful method for determination of the biogenic fraction.

Different measurement techniques (developed for the radiocarbon dating application) can be successfully applied also for the purpose of biogenic fraction determination. Methods differ in complexity and the required mass of a sample, precision and costs.

The innovative 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.

Lowest detectable biogenic fraction is 0.5 %.

The method still needs some improvements, especially for highly quenched liquids, but it gives comparable results with other data evaluation techniques.