# Optimization of the direct LSC method for determination of biogenic component in liquids by applying $^{14}C$

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## Carbon on Earth

$^{12}C$: 98.89 %

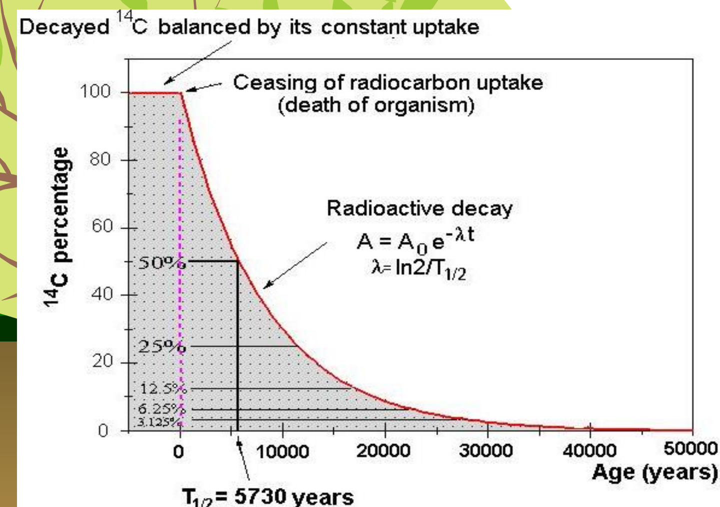
$^{13}C$: 1.1 %

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

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

$O_2$

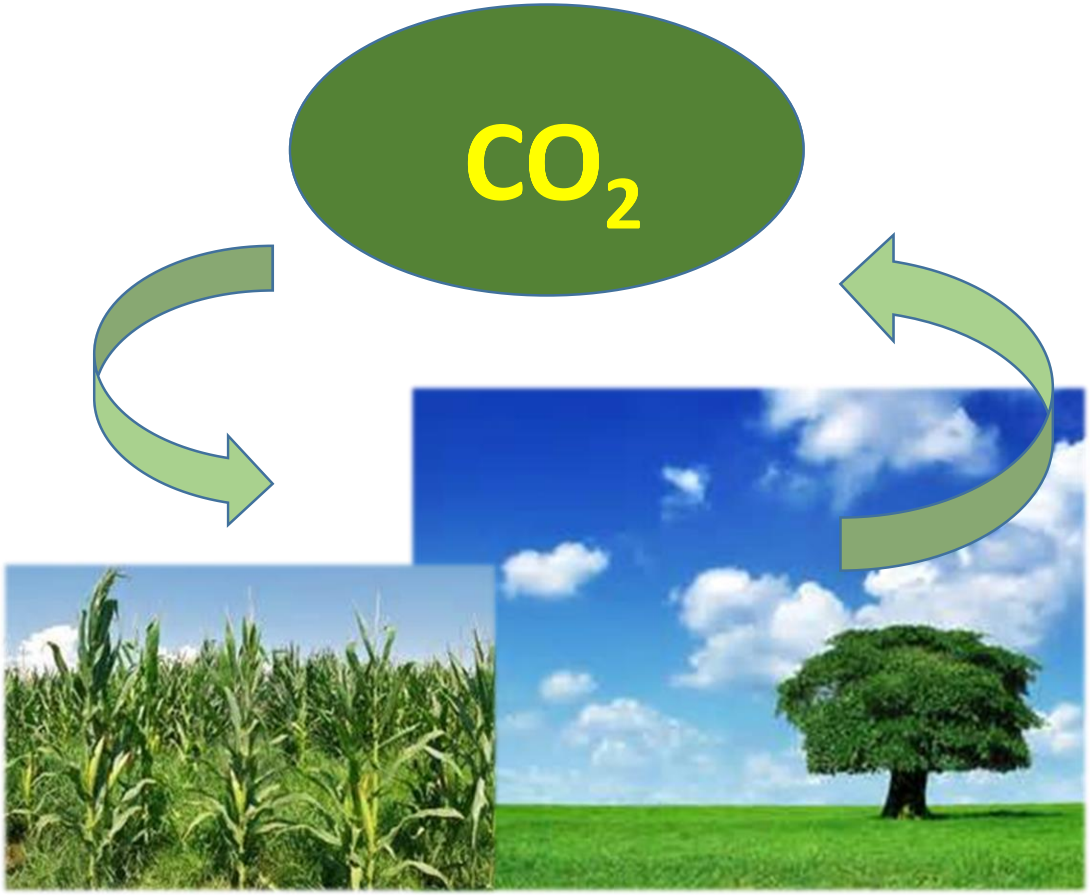
$^{14}CO_2$




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

# Carbon cycle

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




**Biogenic carbon**

All carbon isotopes take part

$^{12}C$: 98.89 %

$^{13}C$: 1.1 %

$^{14}C$: $1.18 \times 10^{-10}$ %

# 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 ‰

- Fast, accurate and reliable method of biogenic component determination in various materials (including liquid fuels) is the method based on radiocarbon, $^{14}C$
- Various measurement techniques can be used
- The method principle – different $^{14}C$ activities in two components – biogenic and fossil
- biogenic component reflects atmospheric $^{14}C$ activity, there is no $^{14}C$ in fossil component

**Fossil matrix** of the fuels is either gasoline (benzine, petrol) or diesel (gas oil)
**biogenic components/blends - biofuels** are usually bioethanol, biodiesel, biogas, biomethanol, biodimethylether, bio-ETBE (ethyl-tertio-butyl-ether), bio-MTBE (methyl-tertio-butyl-ether), fatty acid methyl esters (FAMEs), hydrogenated vegetable oil (HVO), synthetic biofuels, biohydrogen and pure vegetable oil.

## 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

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

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

**Advantage:**

Fast sample preparation

Low cost

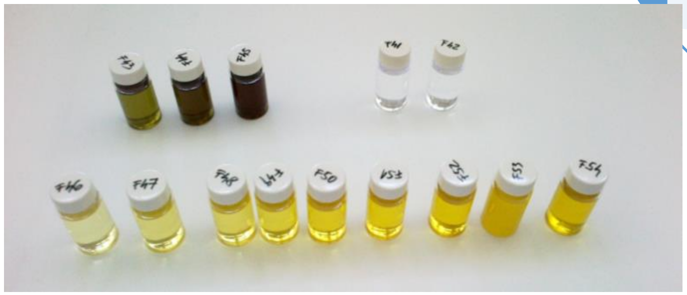
**Problems:**

Not standardized yet

Higher uncertainty

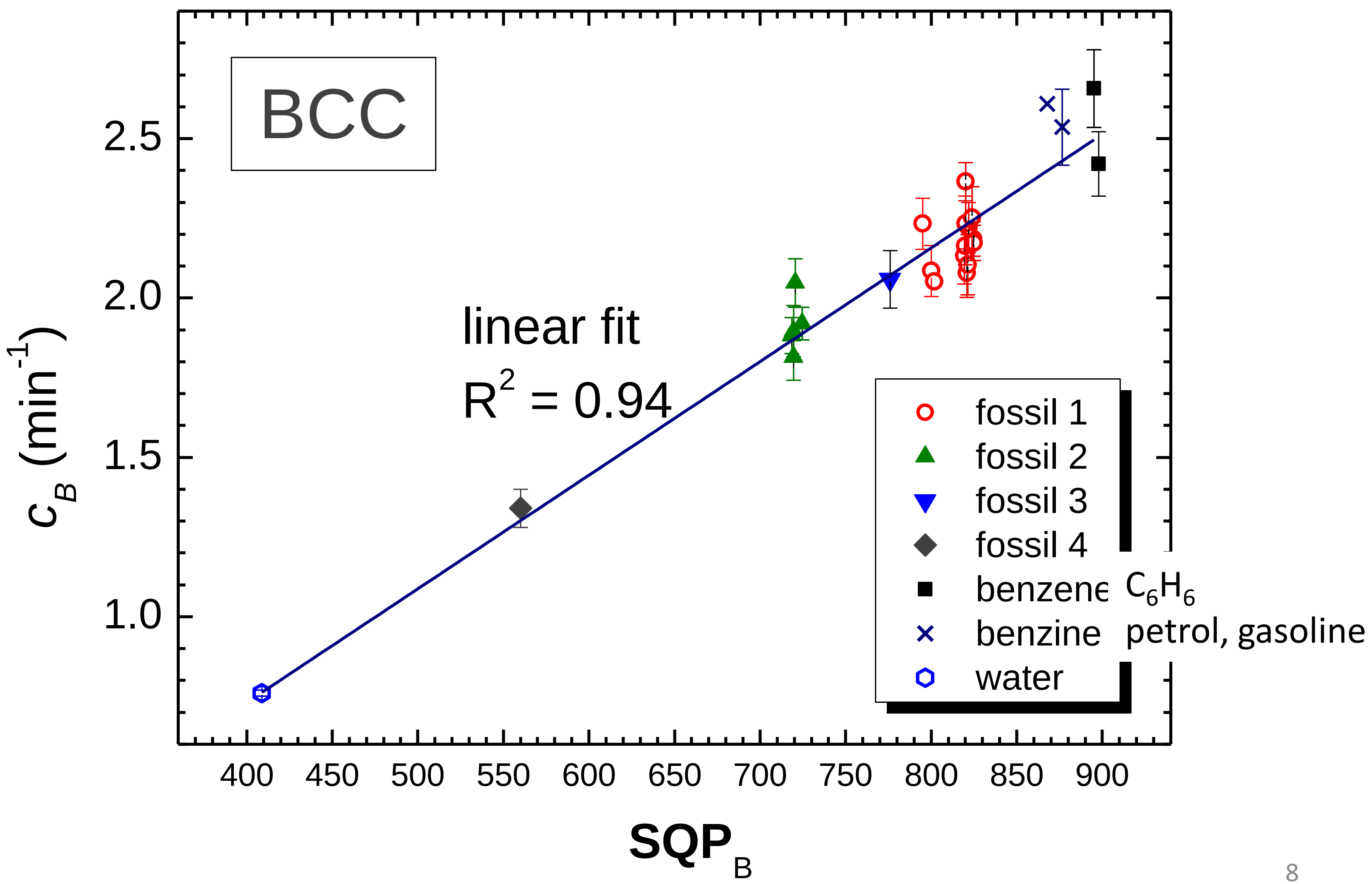
Color quenching

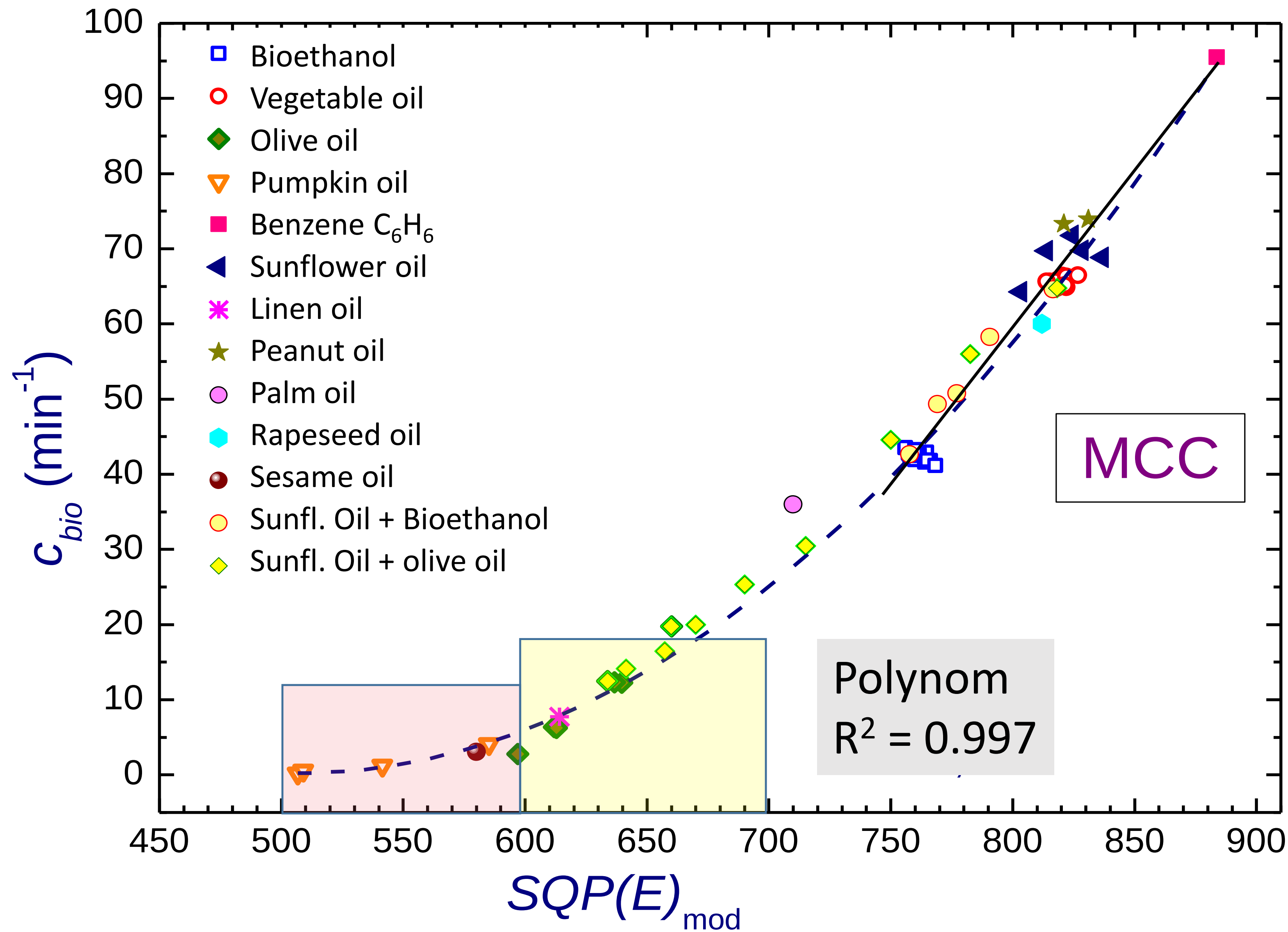
A large variety of mixtures
fossil matrix + biogenic blend



# Background calibration curve (BCC)

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






**Comparison of various biogenic oil samples with the modern calibration curve MCC. All samples are supposed to be 100%-biogenic.**

## Intercomparison

- In 2018 international  intercomparison study ILC/2018 „Content of biocomponent in liquid fuel samples“ organized by the Institute of Ceramics and Building Materials (Opole, Poland).

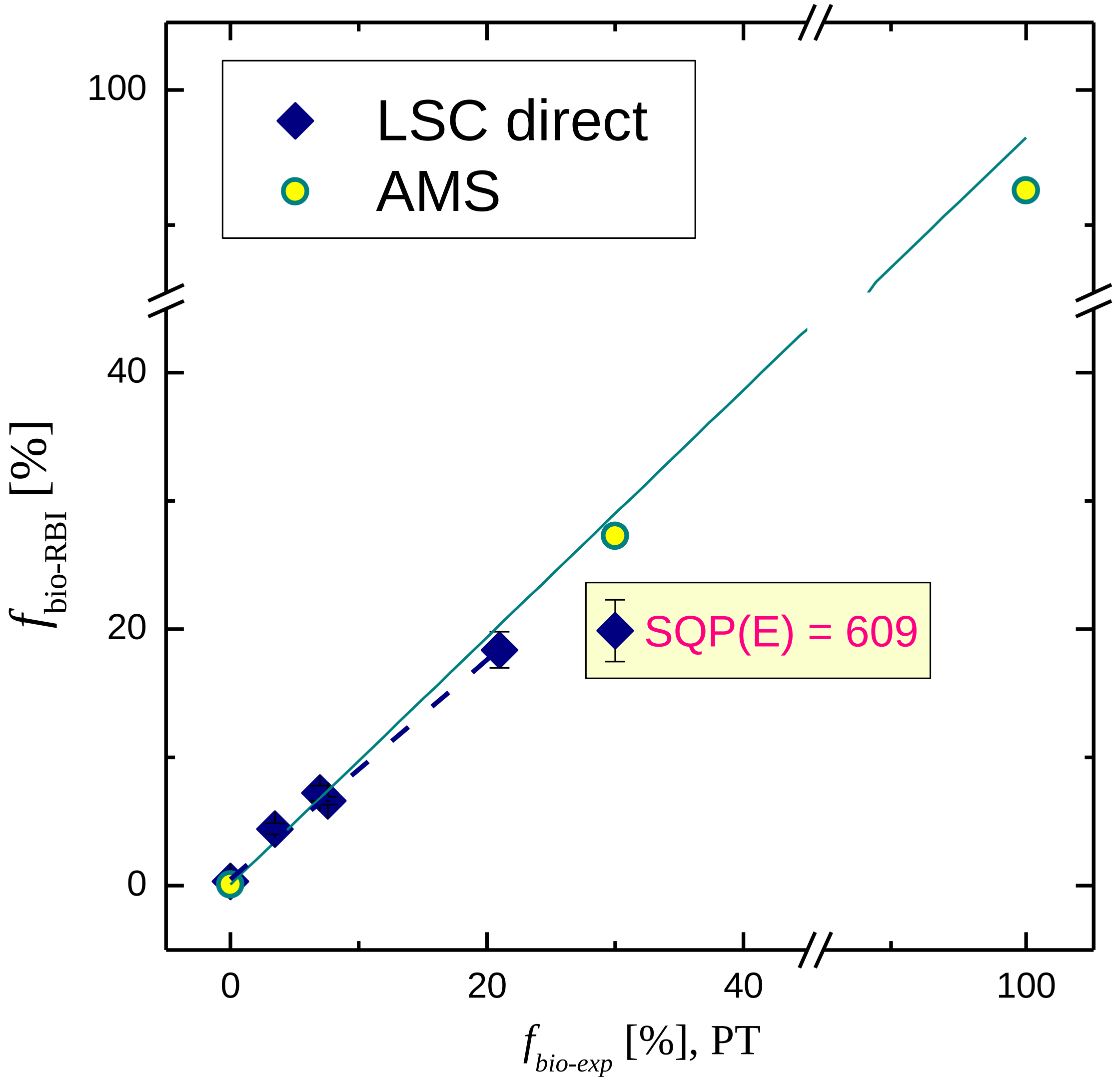

10 mL scintillation cocktail UltimaGold F +
10 mL of sample, glass vials

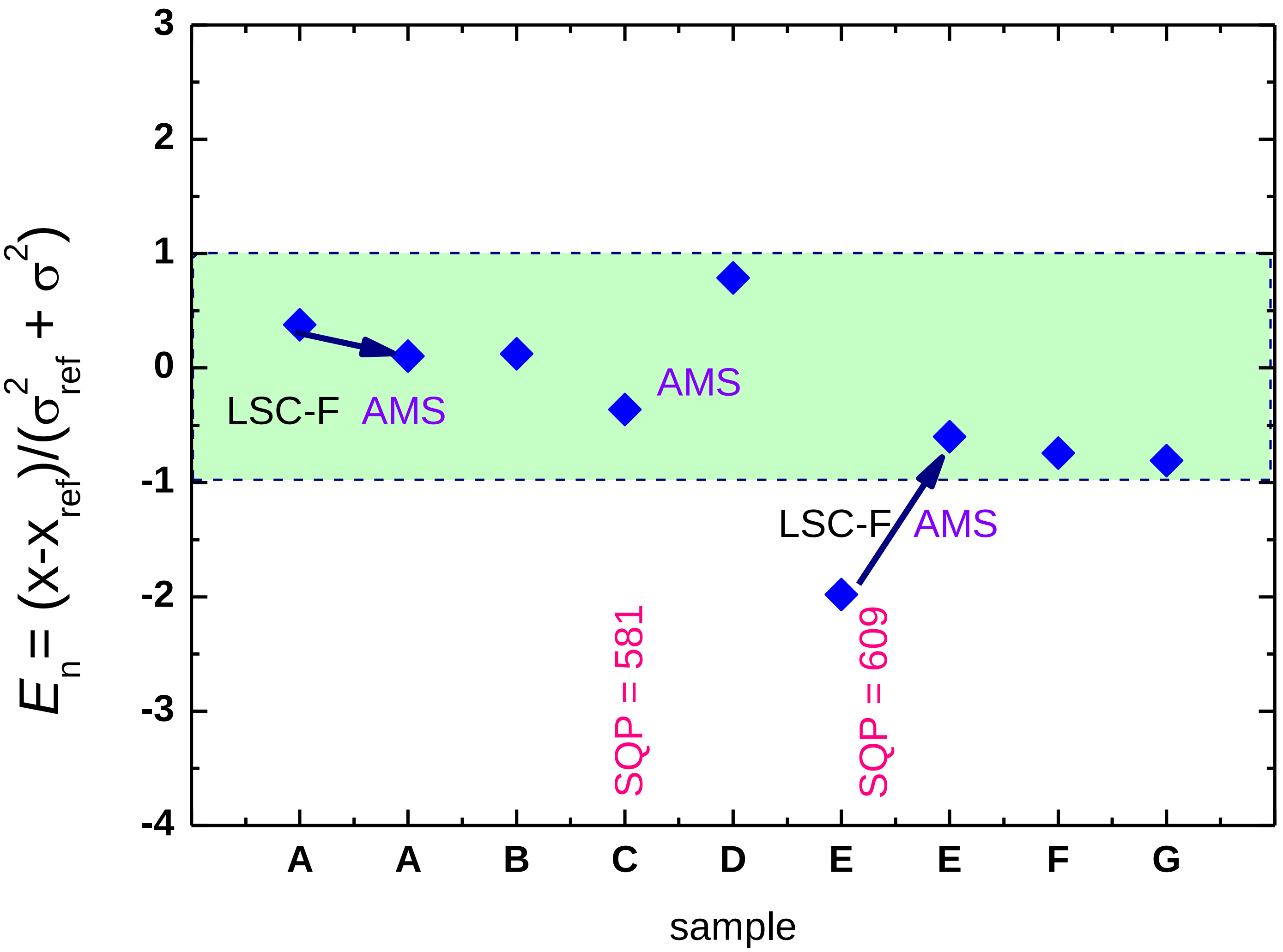
## Intercomparison results

| Sample code | Sample name | *SQP(E)*$_{IRB}$ | Expected $f_{bio-exp}$ [%] | RBI result $f_{bio-IRB}$ [%] |
|---|---|---|---|---|
| **A** | LL/18/0805 | **804** | **0.0** | **0.34 ± 0.25** |
| | | | | **0.09 ± 0.01** [a] |
| **B** | LL/18/0806 | **724** | **7.0** | **7.23 + 0.60** |
| **C** | LL/18/0807 | **581** | **100.0** | **--** |
| | | | | **92.58 ± 0.25** [a] |
| **D** | LL/18/1264 | **758** | **3.5** | **4.44 ± 0.43** |
| **E** | LL/18/1265 | **609** | **30.0** | **19.9 ± 2.4** |
| | | | | **27.3 ± 0.1** [a] |
| **F** | LL/18/1266 | **648** | **21.0** | **18.4 ± 1.4** |
| **G** | LL/18/1267 | **872** | **7.6** | **6.64 ± 0.30** |

a – AMS

## Intercomparison

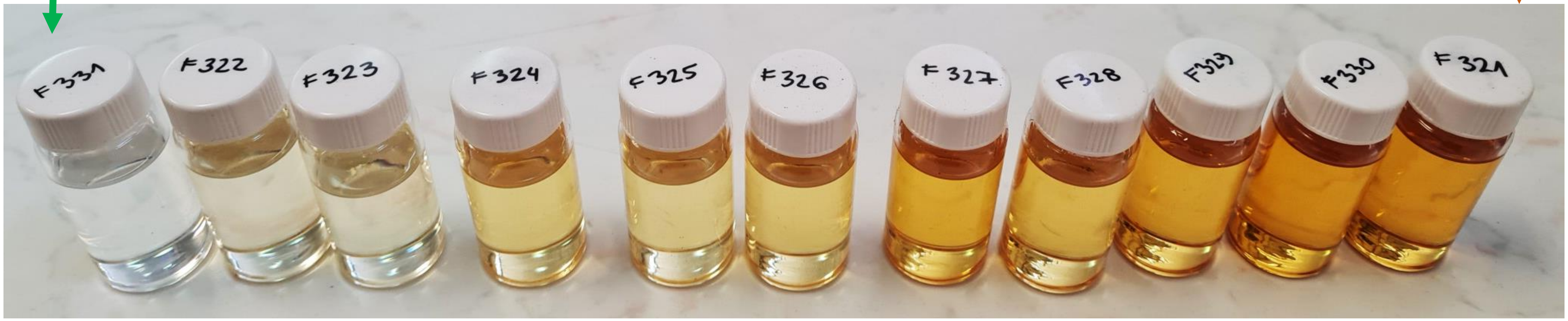





The obtained results justified previously defined limits of applicability of the direct-LSC method for both quantitative (**SQP(E) > 700**) and qualitative results (**600 < SQP(E) < 700**).

## Further validation and optimization of the direct LSC method:

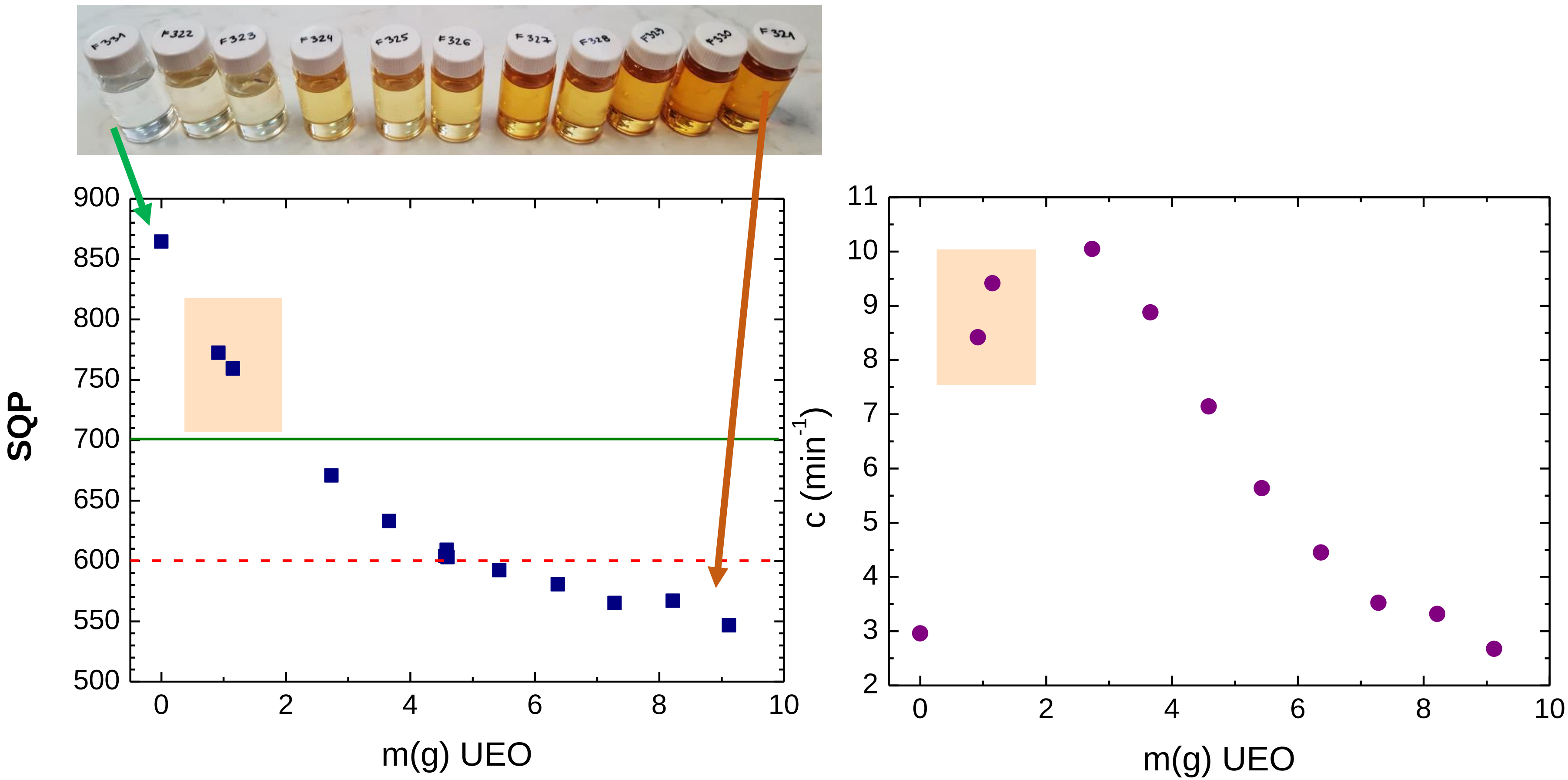
- Z-7226 - **used edible oil** (UEO) was used to test these limits, **SQP(E) = 546**
- AMS: $f_{bio}$ = 97.9 ± 0.3 % (and $\delta^{13}C$ = -29.6 ‰).
- We mixed the UEO with the (fossil) petrol (benzine ) sample (Z-6266, background sample ***f*_bio = 0 %,** good quenching properties **SQP(E) = 864**).
- We monitored changes in the SQP(E), cpm and $f_{bio}$ values in UEO-petrol mixtures in the concentration range 0 – 100 %. The total mixture volume was 10 mL and 10 mL of Ultima Gold F scintillation cocktail was added.



Mixtures of 10 % and 20 % of UEO: SQP(E) > 700

Mixtures containing 30 – 50 % of UEO: SQP(E) > 600

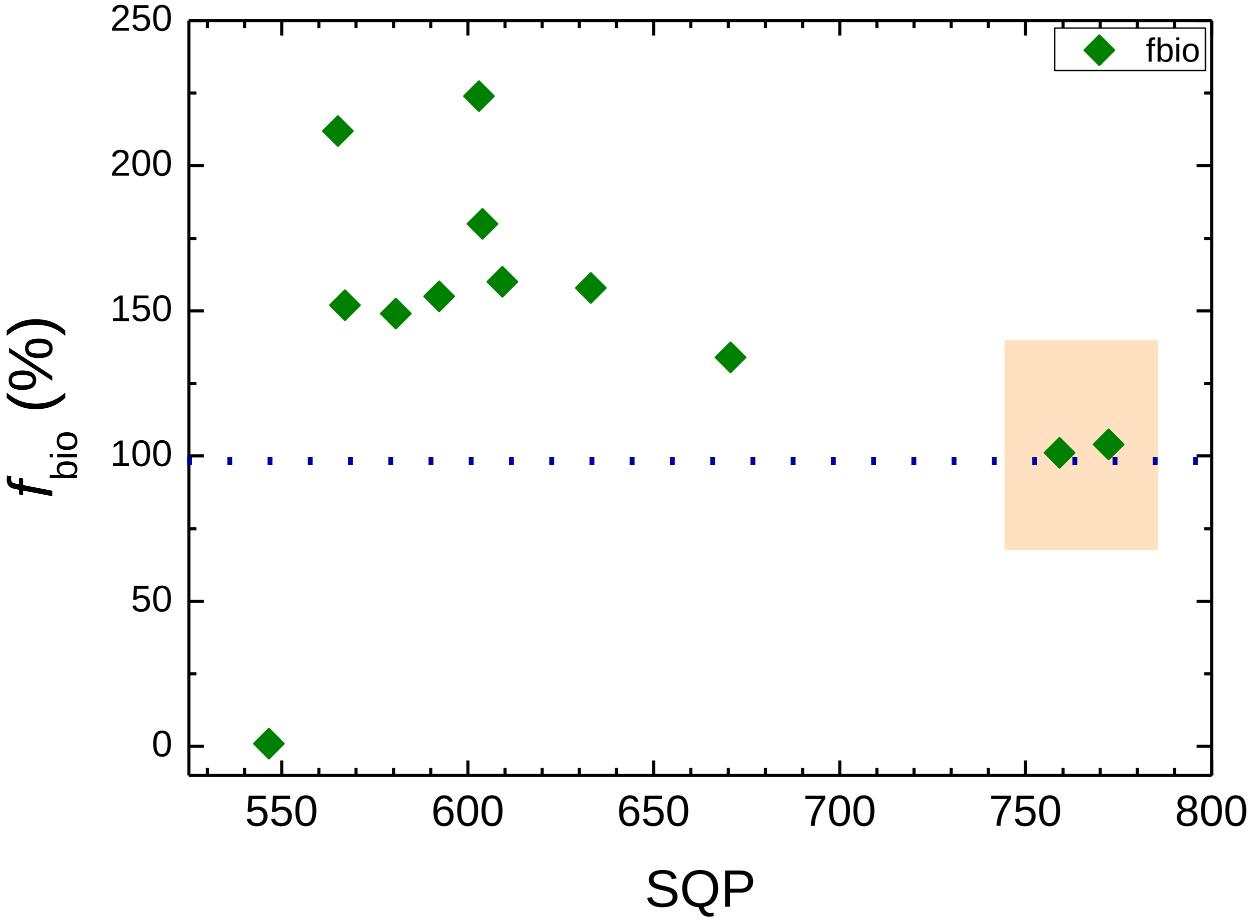
Mixtures containing more than 60 % of UEO: SQP(E) < 600



SQP(E) > 700 → $f_{bio}$ was 104.0 ± 1.2 % and 101.1 ± 1.3 %, in acceptable agreement with AMS 97.9 ± 0.3 %, confirming the quantitative region of SQP(E)

Mixtures containing 30 – 50 % of UEO → SQP(E) between 671 and 609, $f_{bio}$ ~ 150 %, confirming qualitatively acceptable results.

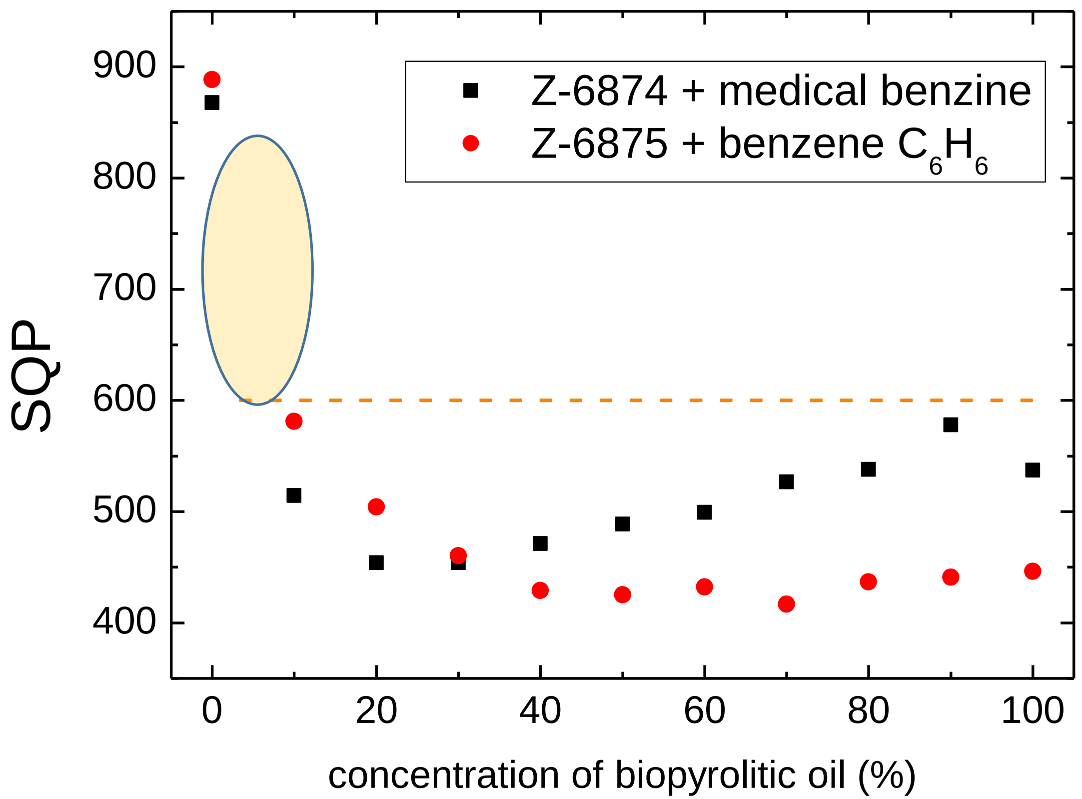
Mixtures >60 % of UEO → SQP < 600 and $f_{bio}$ values had a large spread.



Additional tests:

Z-6874 biopyrolitic oil #1, SQP = 537, with medical benzine, SQP = 867

Z-6875 biopyrolitic oil #2, SQP = 446, with commercial benzene $C_6H_6$, SQP = 888




All mixtures SQP < 600,

plan for mixtures with < 10% biopyrolitic oil

# Conclusion

Determination of the biogenic fraction in various materials (liquid fuels especially) is an interesting topic for the scientists, for various industries and for the global environment.

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.

The method gives comparable results with other data evaluation techniques, as shown by the intercomparison results.

The results are quantitatively good for SQP > 700.

Qualitative results are obtained for 600 < SQP < 700.

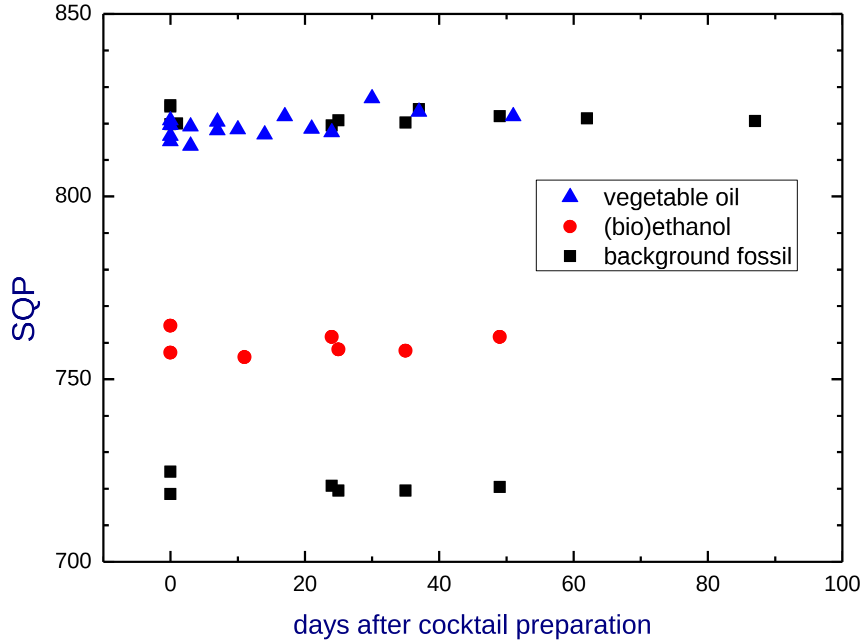
When SQP < 600,  other techniques should be used (AMS).

In progress, test of mixtures with $^{14}C$–free samples with high SQP values.

*Thank you*

## Next to study

- Influence of aging of both original mixtures and prepared scintillation cocktails on SQP and count rate will be studied




- Bio-pyrolytic oils – dark, not dissolvable in custom organic solvents – application of AMS