Determination of biogenic fraction in solid and liquid fuel by the ^{14}C method

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WHY?

- Search for alternative energy sources (not fossil fuels)
- Reduce emission of CO_2 from fossil fuels
- Production of energy from biogenic material (sugar cane, rape, corn etc.)
- EU “environmentaly kind politics” - stimulation of use and production of biofuel by lower excise and income tax relief - EU directives require a minimum amount of biogenic material (bio-ethanol) in fuel – need for control of producers and dealers

HOW?

- Need of simple, fast, reliable, sensitive, accurate, not expensive … method
- bio-fuels can be distinguished from fossil fuels by their ^{14}C activity (bio-fuels reflect the ^{14}C activity of the atmosphere during the growth period, fossil fuels do not contain ^{14}C)
- Possibility to use AMS or LSC methods as for dating [1,2]
- Direct measurement of liquid fuels LSC

1. G A Norton and S L Devlin: Bioresource Technology 97 (2006) 2084
2. Noakes et al, A comparison of analytical methods…, in LSC 2005, Advances in Liquid Scintillation Spectrometry, 2006, p.259–271

Comparison of various ^{14}C measurement techniques

Code	Method description	Advantage	Disadvantage
LSC-A	absorption of CO_2 in Carbosorb® E + Permafluor® E	low cost, relatively simple	limited sample capacity (~0.6 g C) larger uncertainties (~2 pMC) not sensitive for low ^{14}C activities
LSC-B	benzene synthesis	High sensitivity, good precision (~0.5 pMC)	time-consuming sample preparation, low capacity
AMS	graphite targets	High sensitivity, very precise (~0.2 pMC)	high cost, homogeneous samples?
LSC-F	only liquids with UltimaGold F	no sample preparation, low cost	not yet standardized, color quenching, sensitivity?

Direct measurement of (liquid) fuels in LSC

Advantages:

Fast sample preparation

Low analysis cost

Problems:

Not standardized

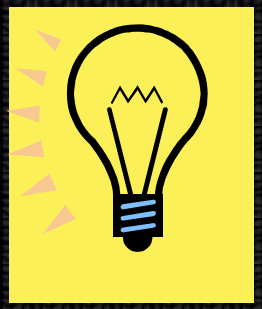
Higher uncertainty

Problem of quenching (color)

Various blends in different matrices

- commercial mixtures for quench curve determination
- Different colors of fuels cause problems (SQP, efficiency)
- use of various method of decolorization
- use of ^{14}C spikes, or ^{14}C-labeled material
- apply different/complicated evaluation methods for various matrices/blends

We were looking for simple, robust and yet accurate technique that will depend neither on the matrix nor on the blend

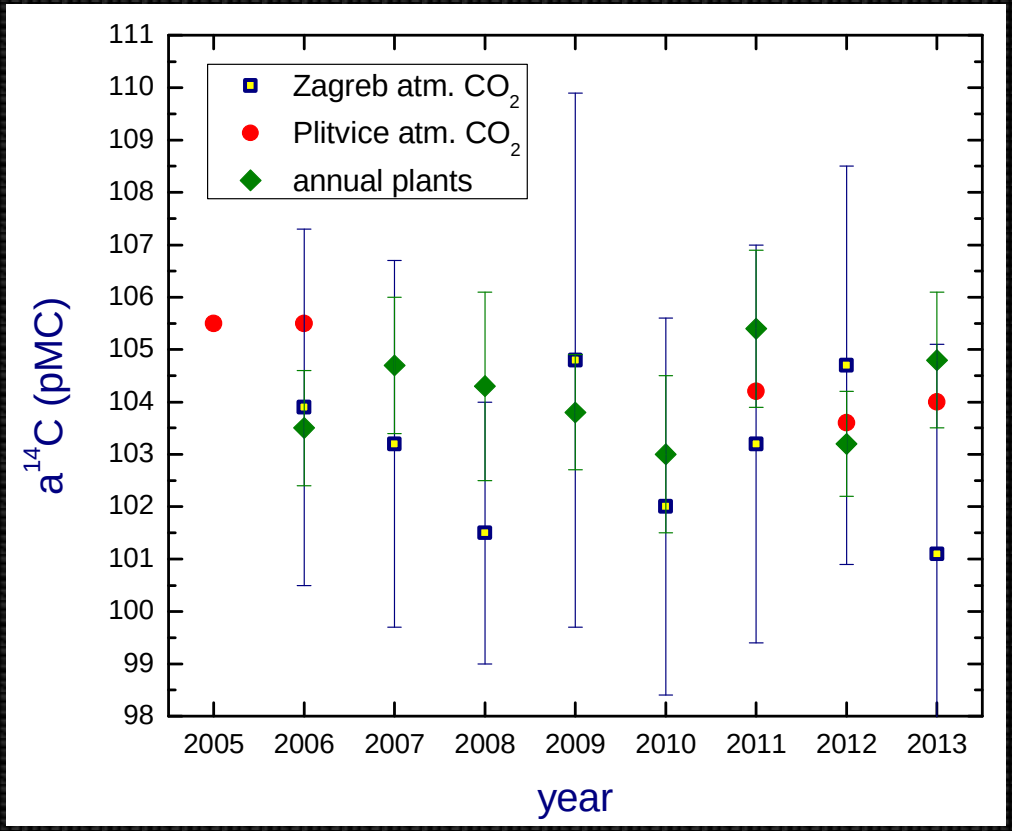


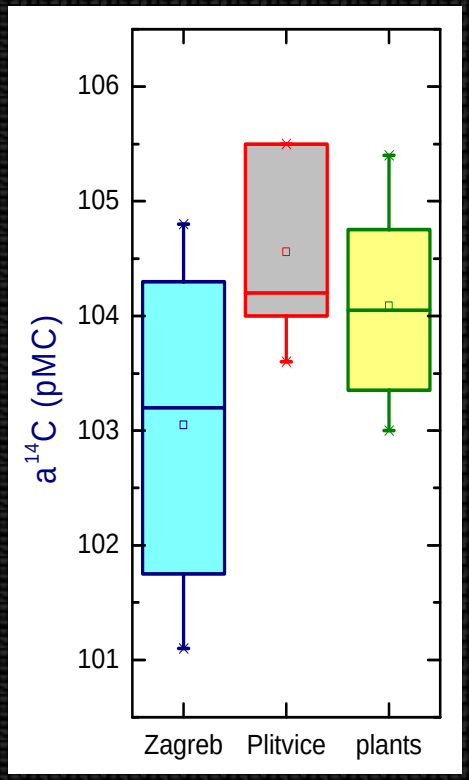
Idea!

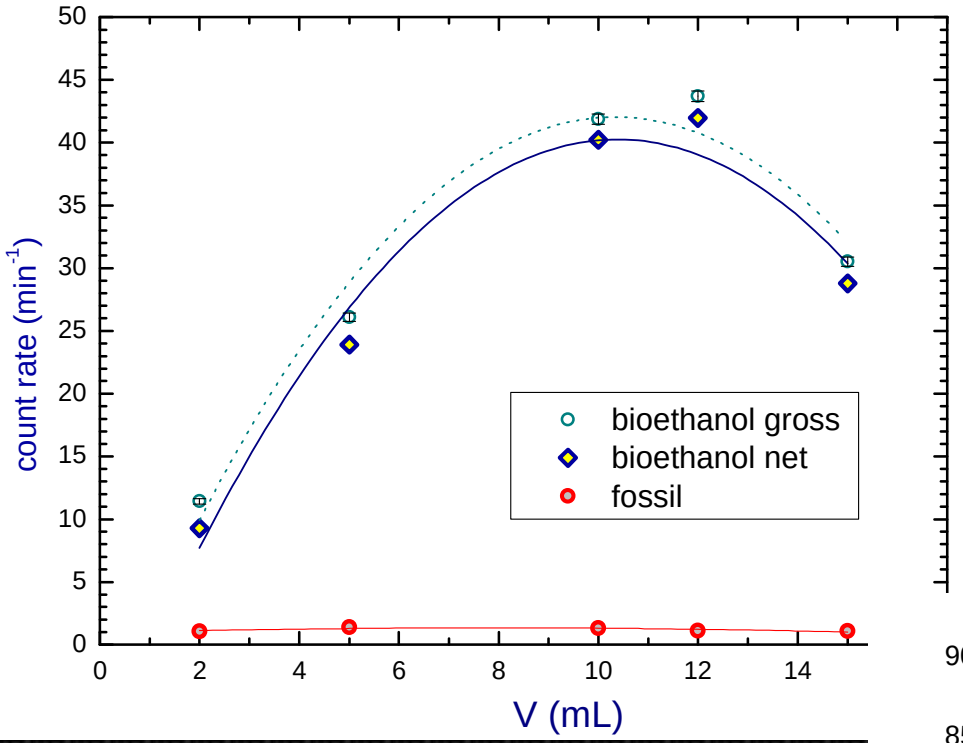
Convert a problem to an advantage:
use various biogenic (100% biogenic) compounds of different colors and quenching properties to construct the "modern calibration curve" (MCC), i.e. the curve relating the SQP parameter and the net count rate of biogenic compounds.

But, several questions need answers!

- any derivative of short rotation crops can be used (harvesting year should be known) as modern standard
- mean ^{14}C activity of the atmosphere has not significantly changed over last 10 years → biogenic material produced in this period has also constant ^{14}C activity → no need to know the exact ^{14}C activity of modern biogenic material
- ISO 13833/ADSM D6866: ^{14}C activity of modern biogenic fuels is taken/defined as 105 pMC, or 1.05*226 Bq/kgC

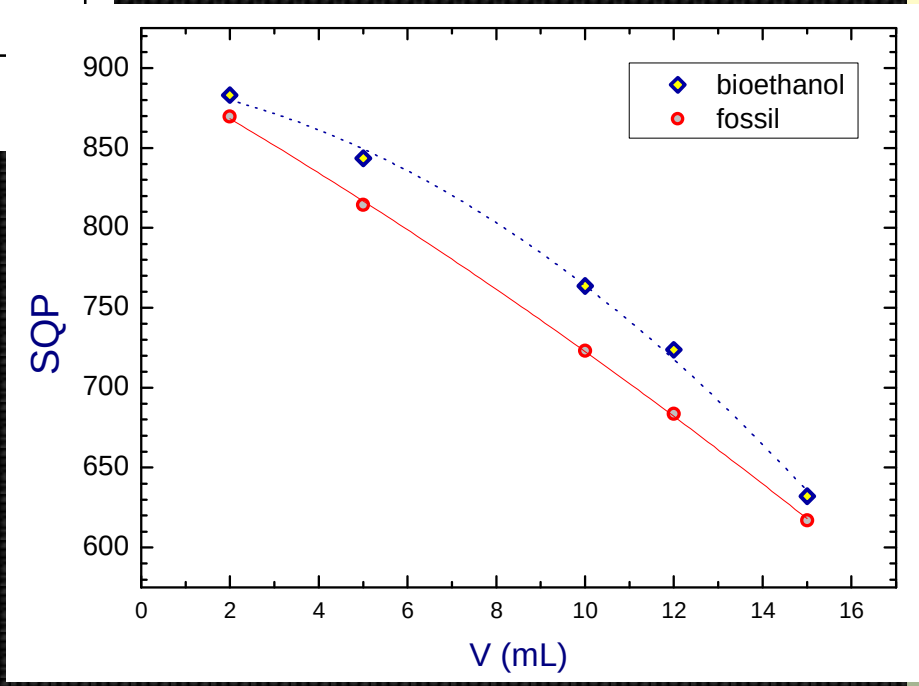






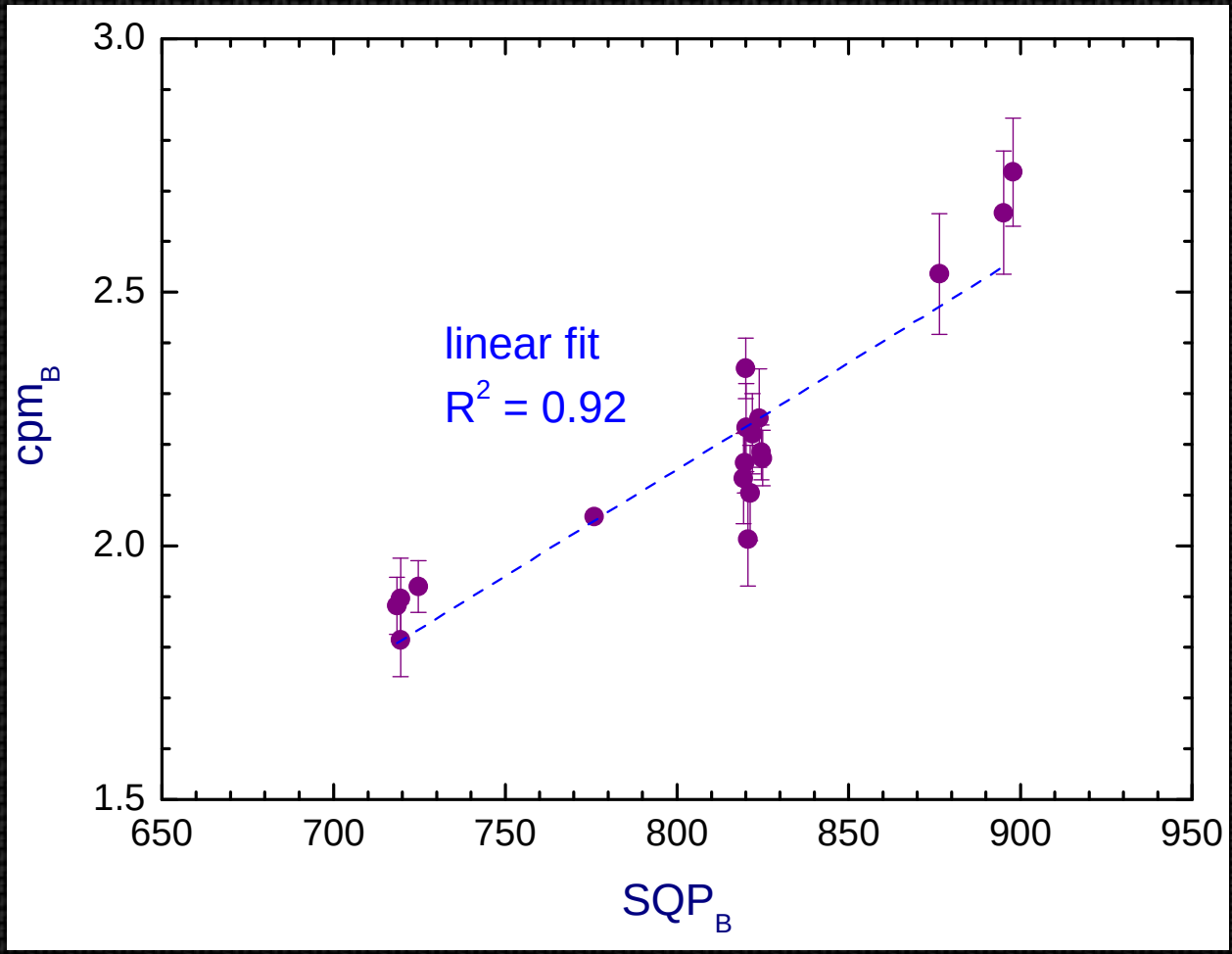
Liquid-scintillator ratio

UltimaGold F
20 mL glass vials
cocktail volume 20 ml
LSC Quantulus
ROI 145 – 570 ch



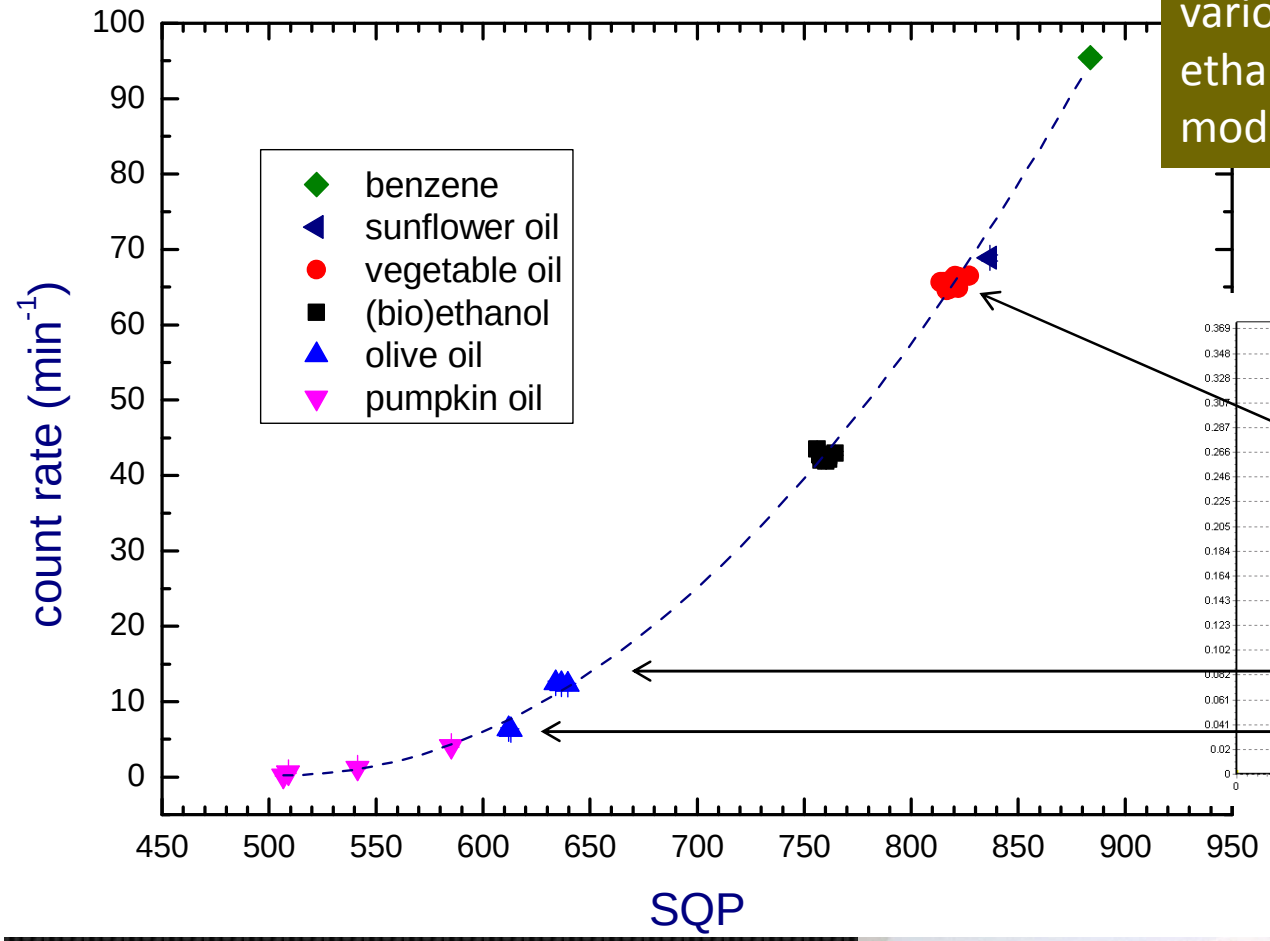
Background calibration curve (BCC)

Various fossil fuels, benzene, benzine

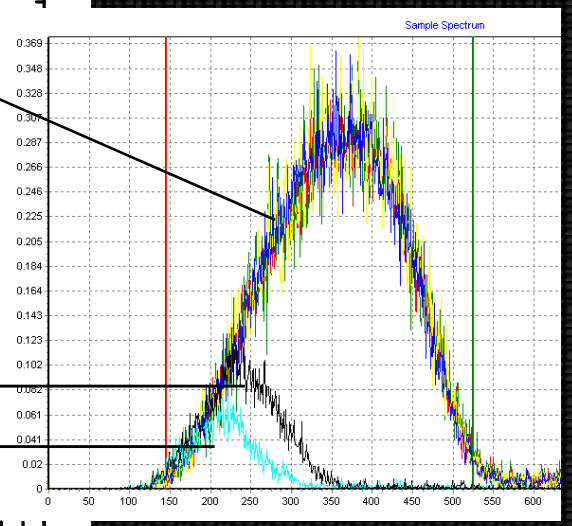


Modern calibration curve (MCC)

modern biogenic samples



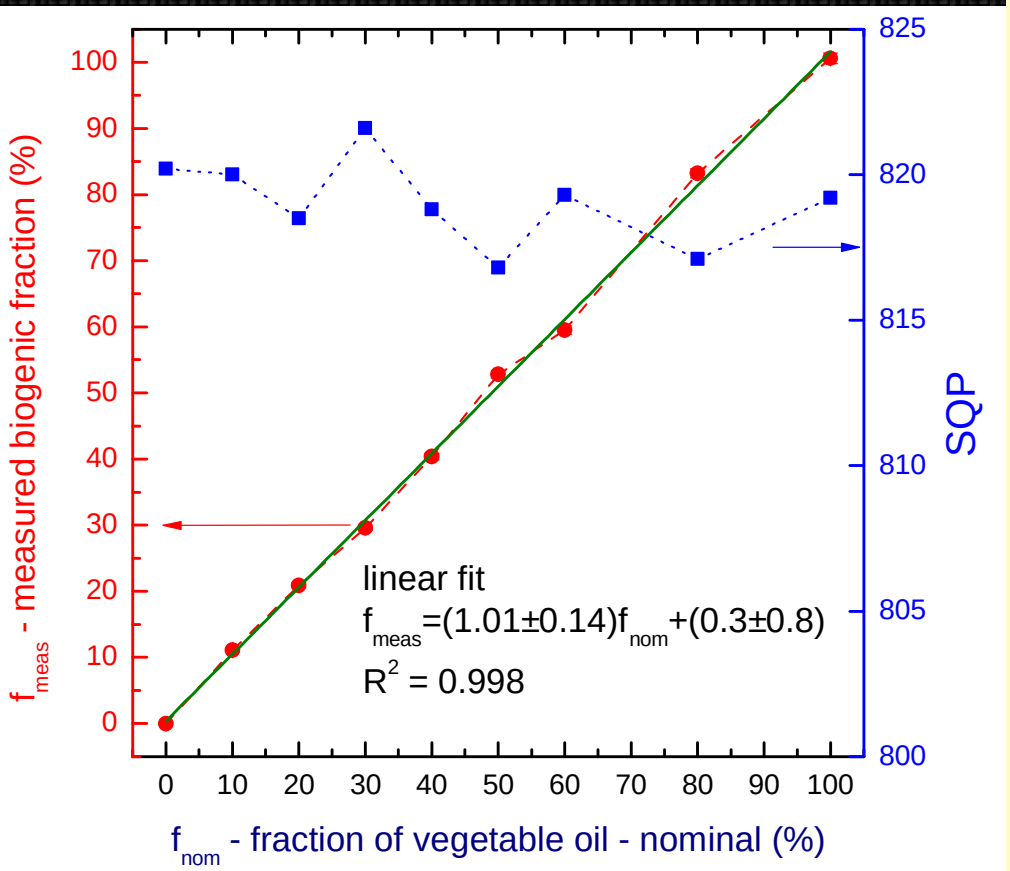
liquids of biogenic origin: various brands of domestic oil, ethanol p.a., benzene (from modern samples)

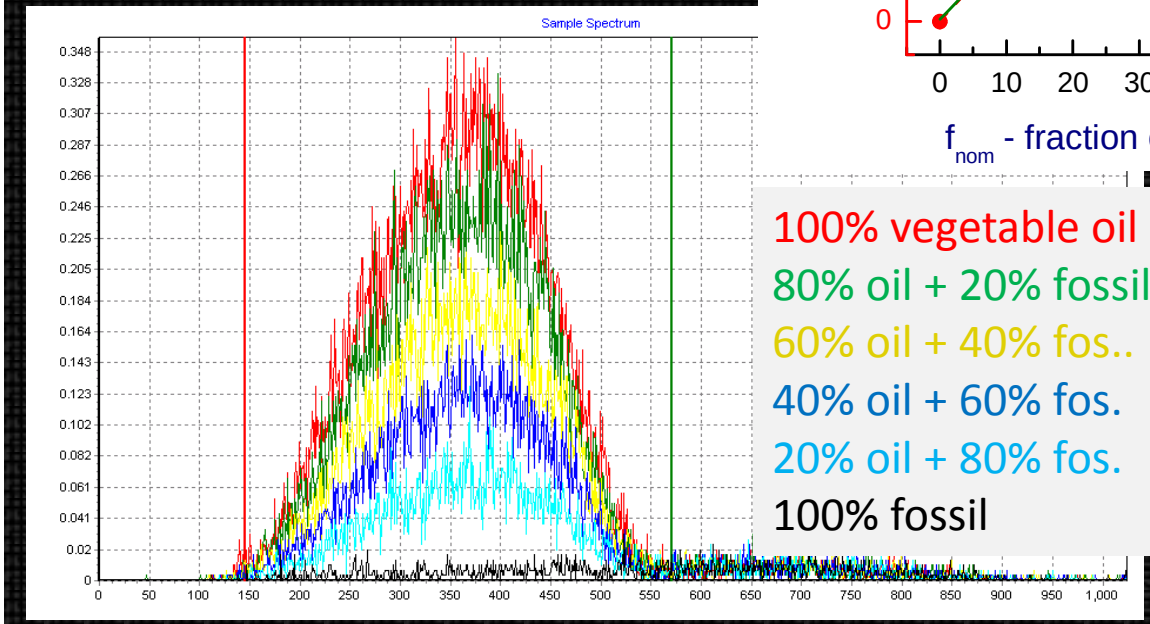


RAD2014

Validation - 1

mixtures of vegetable oil and fossil fuel
app. the same SQP values



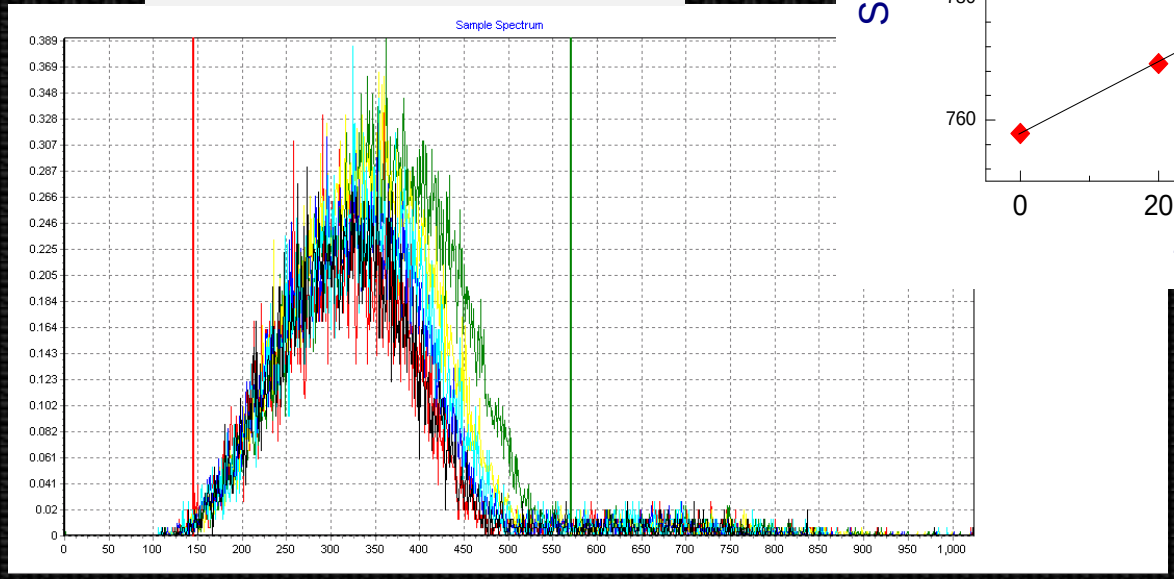


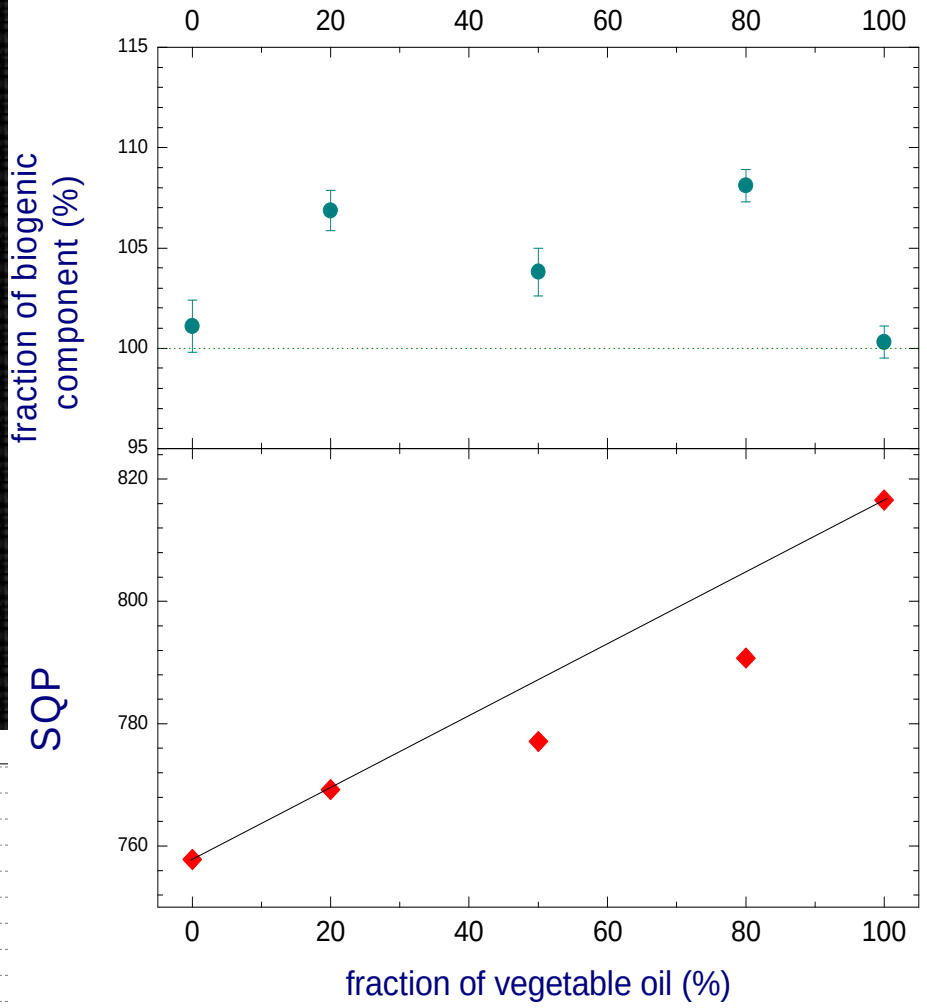
100% vegetable oil
80% oil + 20% fossil
60% oil + 40% fos..
40% oil + 60% fos.
20% oil + 80% fos.
100% fossil

Validation - 2

mixtures of two 100%-biogenic liquids having different SQP values: vegetable oil and ethanol

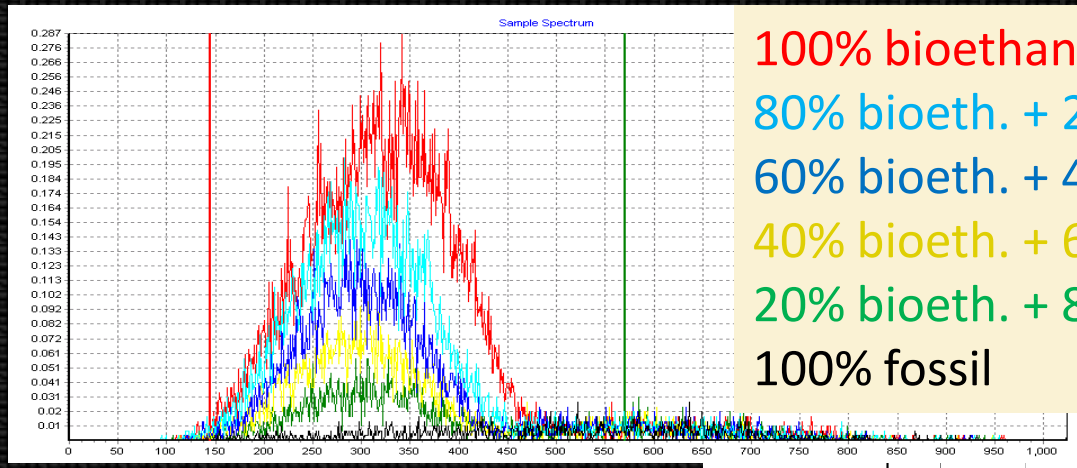
100% vegetable oil
80% oil + 20% bioeth.
50% oil + 50% bioeth.
20% oil + 80% bioeth.
100% bioeth.
100% bioeth. (earlier pr.)



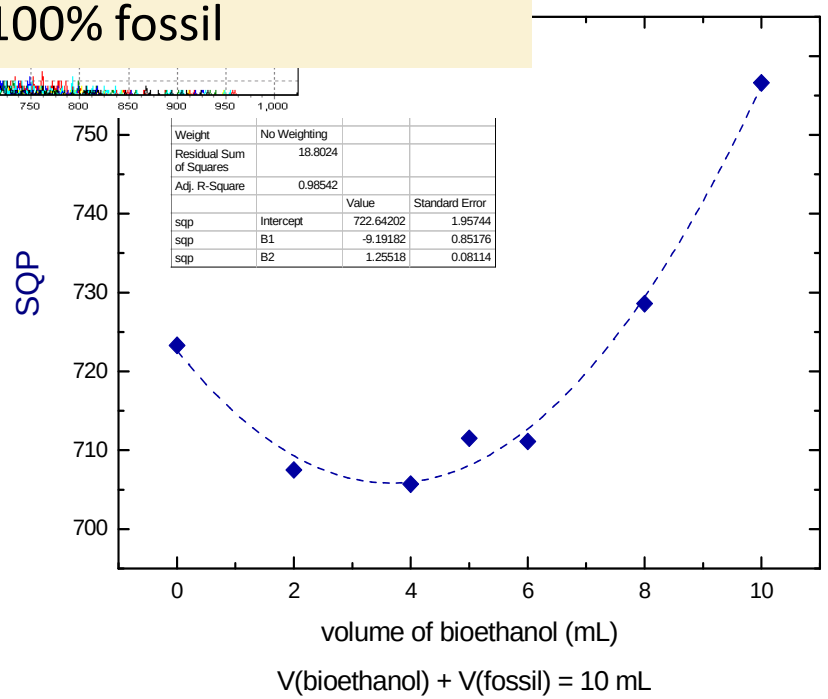


Validation - 3

mixtures of fossil fuel and (bio)ethanol since (bio)ethanol is often used as blend

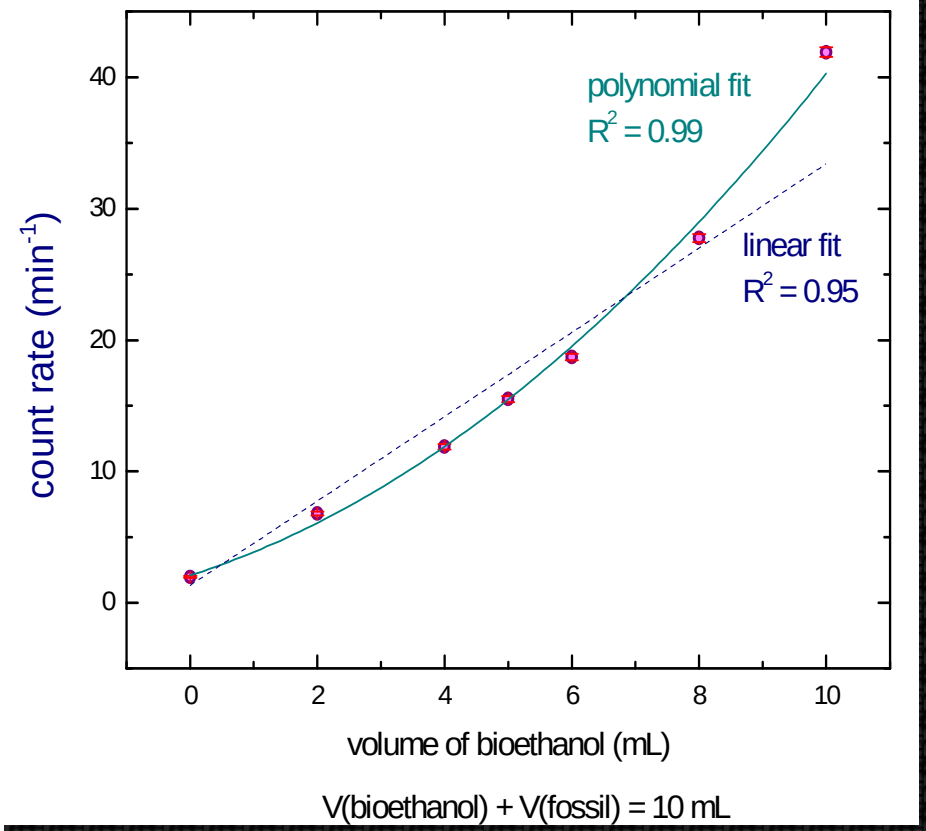


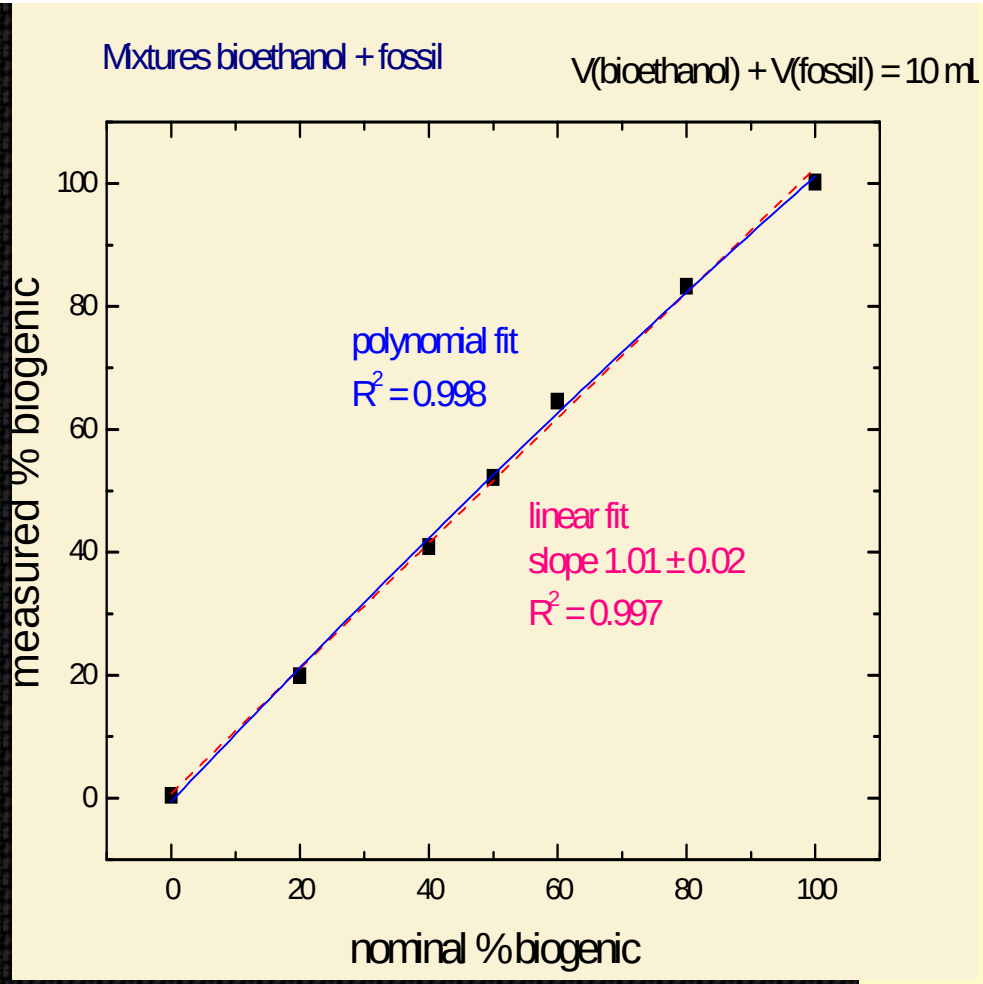
100% bioethanol
80% bioeth. + 20% fossil
60% bioeth. + 40% fos.
40% bioeth. + 60% fos.
20% bioeth. + 80% fos.
100% fossil



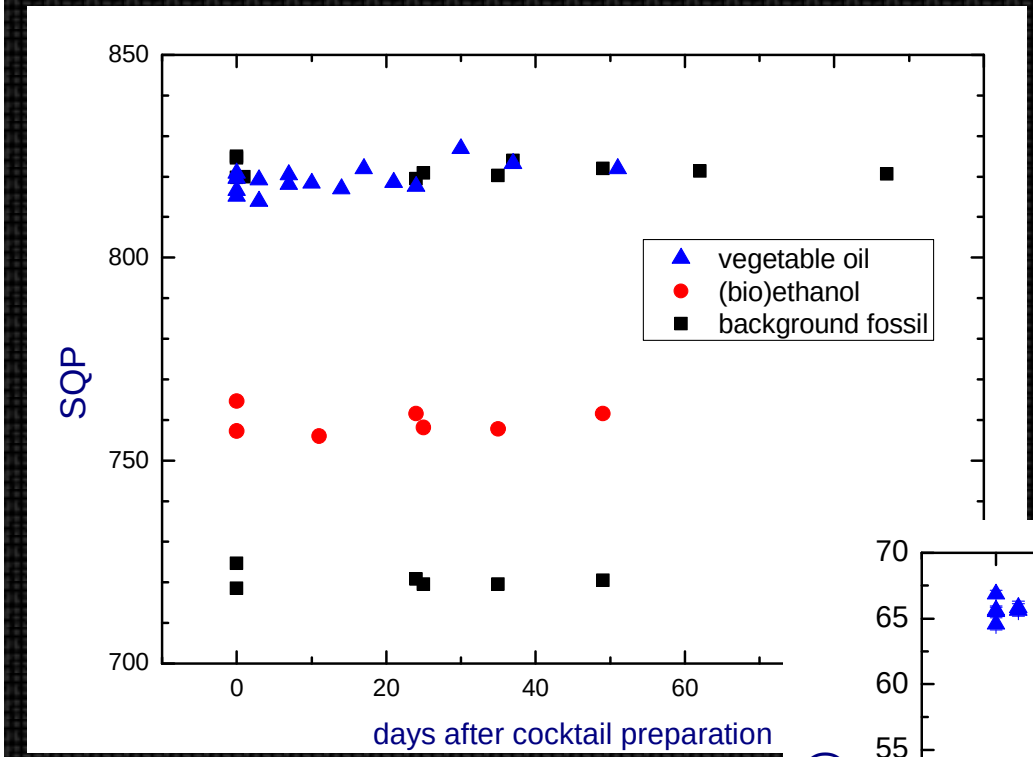
Weight	No Weighting		
Residual Sum of Squares	18.8024		
Adj. R-Square	0.98542		
		Value	Standard Error
sqp	Intercept	722.64202	1.95744
sqp	B1	-9.19182	0.85176
sqp	B2	1.25518	0.08114

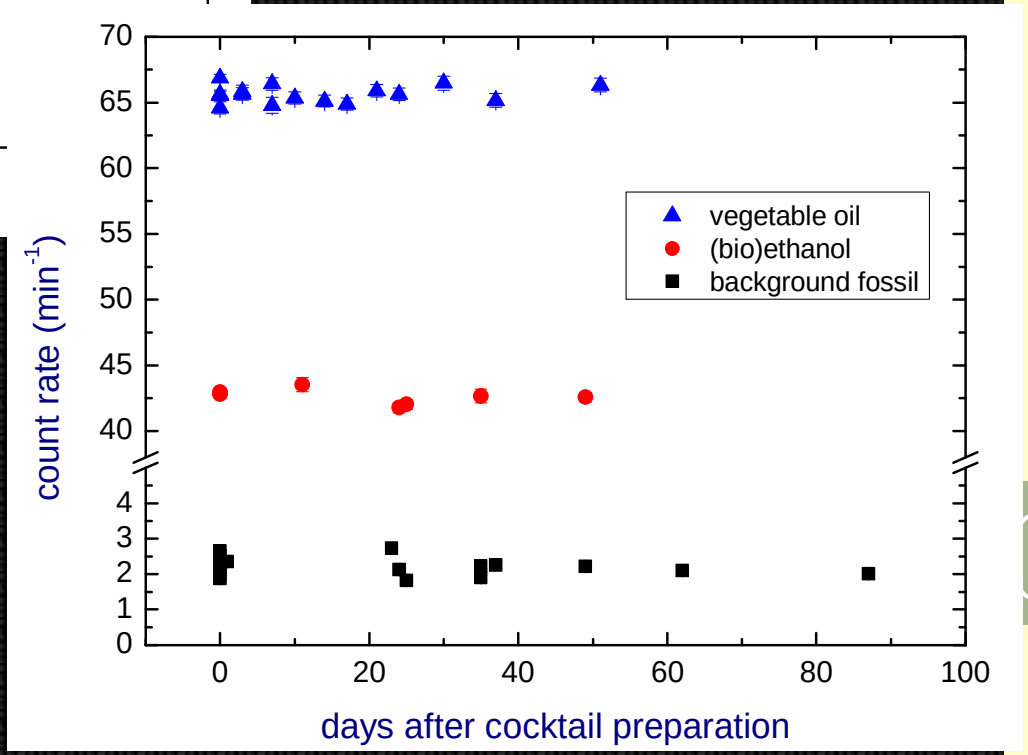
V(bioethanol) + V(fossil) = 10 mL


count rate (min-1)
volume of bioethanol (mL)
polynomial fit
R2 = 0.99
linear fit
R2 = 0.95
V(bioethanol) + V(fossil) = 10 mL


Mixtures bioethanol + fossil
V(bioethanol) + V(fossil) = 10 mL
measured % biogenic
nominal % biogenic
polynomial fit
R2 = 0.998
linear fit
slope 1.01 ± 0.02
R2 = 0.997

Long-term stability of SQP and count rate - aging





Conclusion

- A novel method for determination of fraction of the biogenic component in liquid fuels by measuring their ^{14}C content
- Simple and accurate, color is no more a problem
- Need for intercomparison