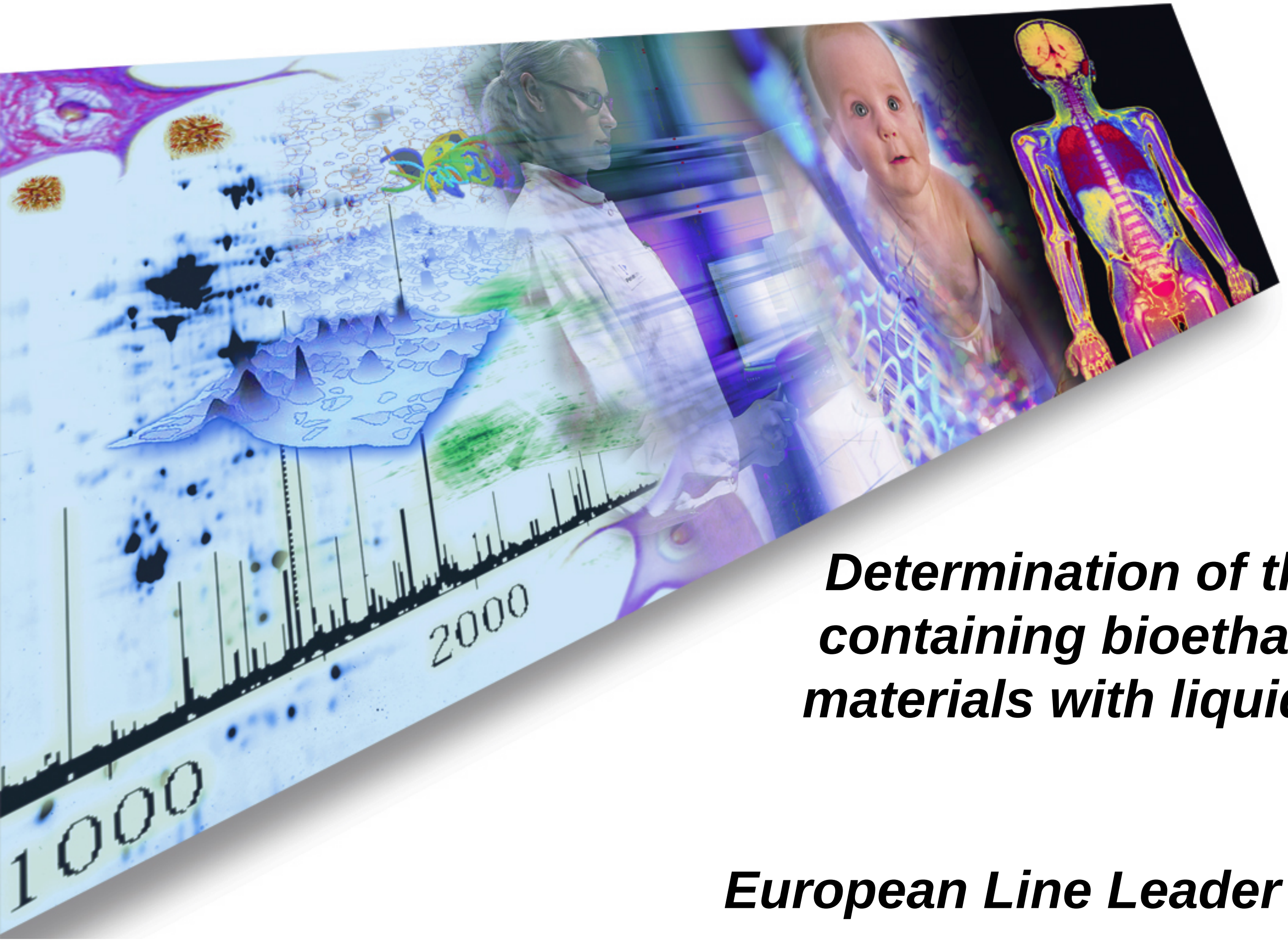

Determination of the 14C content in fuels containing bioethanol and other biogenic materials with liquid scintillation counting

Dr Ronald Edler
European Line Leader Radiometric Detection

Measurements done by:

The measurements of biofuels have mainly been done by Lauri Kaihola and Ronald Edler

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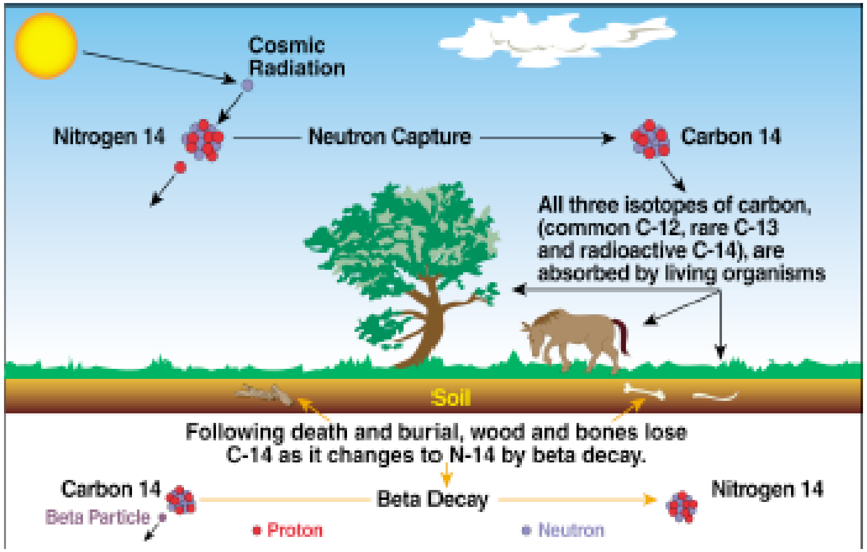
Why is biofuel interesting for LSC?

1. **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).**
2. **To make this change more attractive some countries assess a lower tax for fuels containing biogenic materials. Accordingly, many producers of fuel and custom departments have an interest in determining the amount of biogenic material in fuel.**
3. **Companies with large amounts of CO_2 emissions containing partly biogenic materials can save a lot of money by avoiding CO_2 trading (As a result of Kyoto protocol CO_2 emissions are restricted)**
4. **Biogenic and fossil materials can not be distinguished by classical analytical technologies such as HPLC, GC, IR, UV etc.**
5. **The only difference is the amount of radioactivity (^{14}C, ^{3}H …) which can be measured using LSC or AMS instruments.**

^{14}C life cycle

All living things are naturally labeled with low levels of Carbon-14 produced in the atmosphere

- Cosmic rays naturally produce C-14 in the atmosphere.
- C-14 is quickly oxidized to CO_2 and incorporated into all plants and animals
- C-14 is radioactive (half-life = 5730 years).
- When a plant or animal dies, it no longer replaces its carbon.



- Renewable fuels (ethanol, biodiesel, biogas) are universally labeled (C-14 distributed evenly throughout the molecules).
- Fossil fuels are essentially C-14 free since the carbon has been “dead” and isolated for more than 60,000 years (> 10 half-lives).

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Available Standard Methods

- "ASTM Standard D 6866-06 – Standard Test Methods for Determining the Biobased Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis"

  www.astm.org

  - Method A: Liquid Scintillation Counting (LSC) radiocarbon techniques, max error 15 %, based on CO_2 absorption (Carbosorb/Permafluor)
  - Method B: Accelerator Mass Spectrometry (AMS) and Isotope Ratio Mass Spectrometry (IRMS), errors 1-2 % and 0.1 to 0.5 %, respectively
  - Method C: LSC techniques to quantify biobased content of carbon converted to benzene, error + - 3 %

LSC Analysis

- ASTM Standard D-6866-06

Ch 7.1 describes 'one possible combination' for Method A) in greater detail:

12 mL of Ultima Gold + 6 mL of CarboSorb + 2 mL spectrometer grade methanol. Efficiency should be greater than 75 %

We recommend Carbo-Sorb E +, that can accept up to 4.8 mmol CO_2 per mL, and Permafluor E+ in ratios 1:1 or lower

But still sensitivity is limited

Direct mix of sample and cocktail

- **Organic cocktails accept a wide range of gasoline/ethanol mixtures and biodiesel**
  - **Cocktail: Ultima Gold F or OptiScint HiSafe**
  - **10 mL fuel per 10 mL cocktail (best cocktail/sample ratio for colourless fuels is approx. 8/12)**
  - **Blank sample should be same gasoline/EtOH mixture of fossil origin**
  - **Reference sample should be same gasoline/EtOH mixture of fossil origin or alternatively small amount of dissolvable reference material is later added to the unknown samples to verify their counting efficiencies**

Merits and Drawbacks of the Proposed ^{14}C Analysis Methods

Method	Merit	Drawback
Direct LSC analysis	Minimal, fast sample prep Good sensitivity Lower costs per evaluation High instrument availability worldwide, LSC is the most widely used method for ^{14}C determination	Not in accordance with ASTM standard D6566-06, which discusses Methods A, B and C
Method A: CO_2 & LSC	Less sample prep than in Method C, lower costs per evaluation, high instrument availability worldwide	Small sample activity due to the small amount of carbon accepted by Carbo-Sorb E, not sensitive for the lowest ^{14}C concentrations
Method B: AMS	High sensitivity, precise	High cost, mostly for cases in dispute or less than 10 % carbon by weight
Method C: C_6H_6 & LSC	High sensitivity, precise, high instrument availability worldwide	Slow sample prep, small capacity, new synthesizers hard to acquire, benzene is carcinogenic

Possible Instrumentation……

Two LSC models are suitable for the measurement of these samples, the Quantulus or the 3170TR/SL.

Both instruments have comparable sensitivity for ^{14}C (slight advantage for the Quantulus), however, the 3170TR/SL is easier to use especially for customers without experience in LSC technology.

Quantulus

TriCarb 3170

….using different technologies

Two LSC models are suitable for the measurement of these samples, the Quantulus or the 3170TR/SL.

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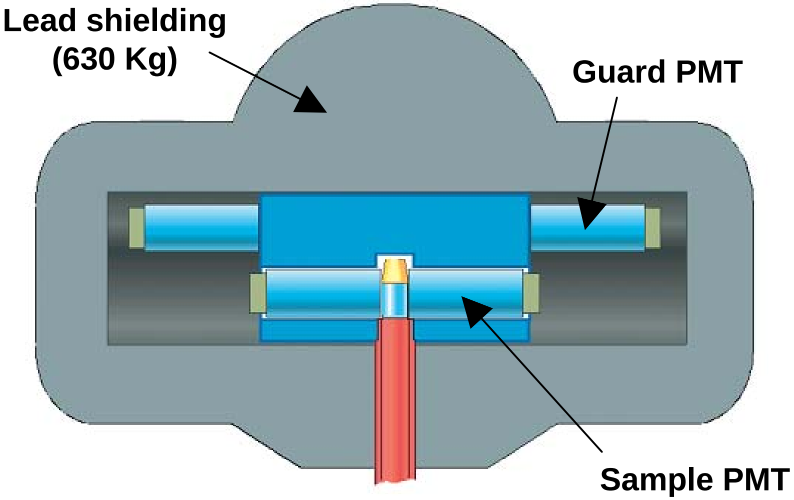


Quantulus

BGO detector and TR-LSC TriCarb 3170

Typical customer

Customers are mainly mineral oil companies and custom departments which never used LSC technology so far.

Most important features for these customers:

Know how transfer and training should be possible within a few days.

Sample preparation should be limited to a minimum and the instrumentation should be easy to use.

Comparison of Methods for Radiocarbon Based Analysis

Method	Sample preparation time	Analysis time min	Analysis cost** (USD)	Instrument cost	Sample size	Contamination risk***	Precision
Direct Liquid Scintillation Counting	3 minutes	330	150	100 kUSD	5-10 g	Low	< 3%
Method A Liquid Scintillation Counting with CO2 trapping*	3 hours	1300	250	150 kUSD	0.2-1 g	Moderate	< 9%
Method B Acceleration Mass Spectrometry (AMS)*	2 hours	20	400	2 MUSD	1 mg	High	< 1%
Method C Liquid Scintillation Counting with Benzene Synthesis*	3 hours	1300	250	150 kUSD	2-10 g	Low	< 2%

* ASTM Standard method

** Includes the depreciation of equipment

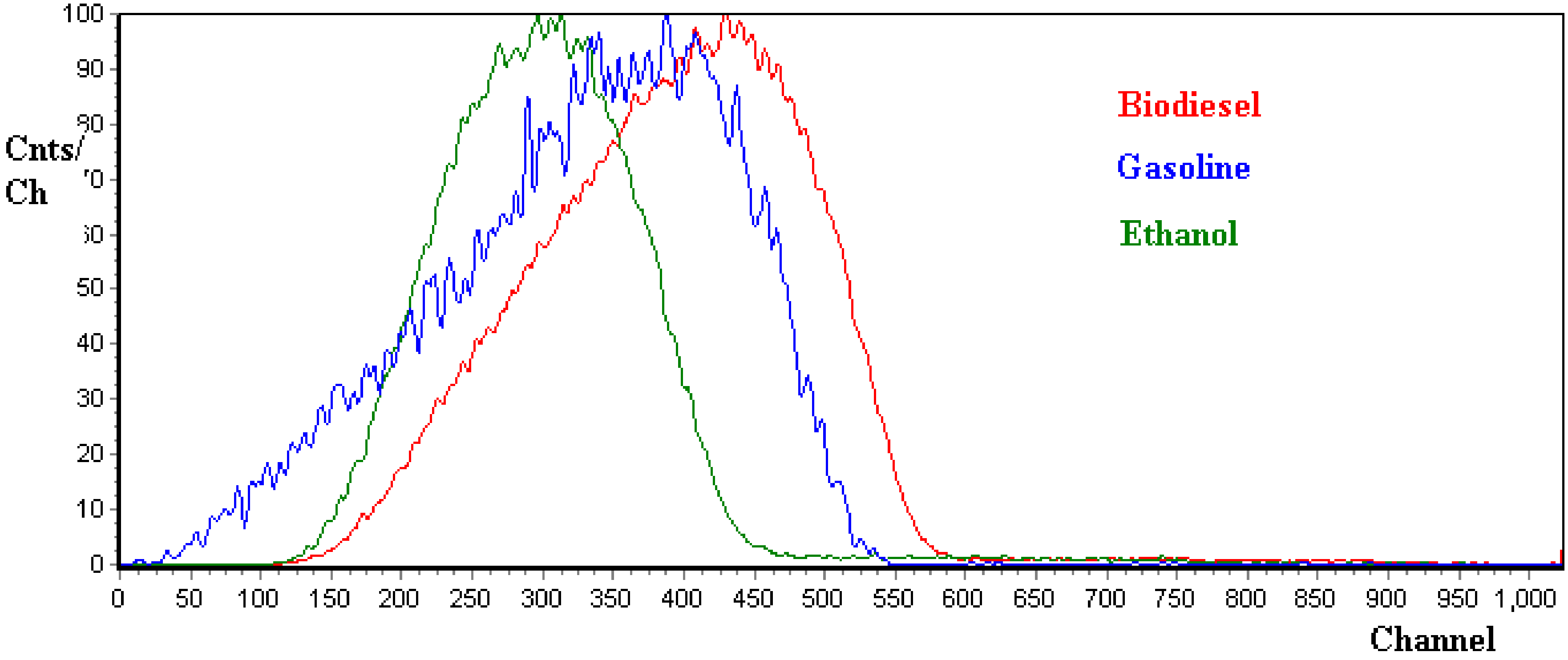
*** Risk of contaminating the sample with ambient biological carbon during the process

^{14}C in Fuels and Pure Ethanol

^{14}C beta spectrum in biodiesel, gasoline/ethanol mixture and pure ethanol

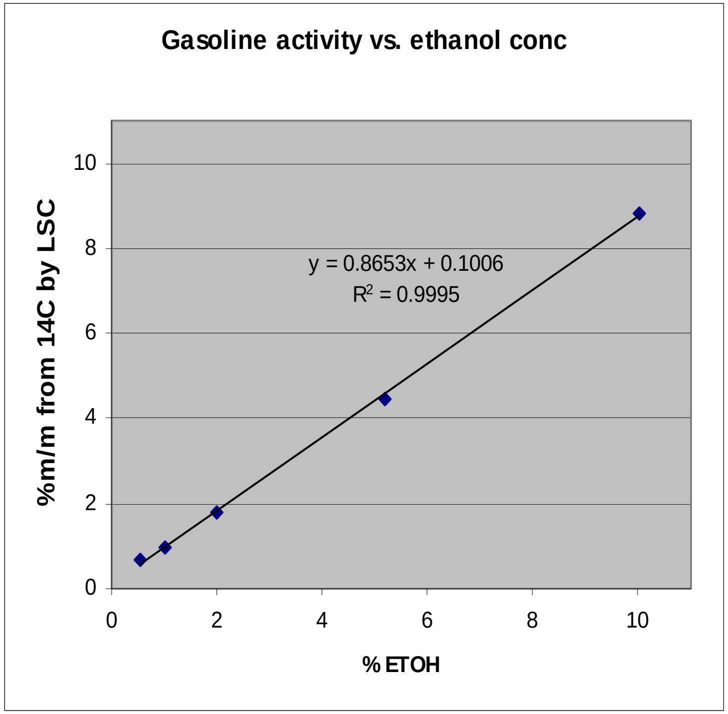
- **gasoline/ethanol measured in Quantulus with low bias, others high**

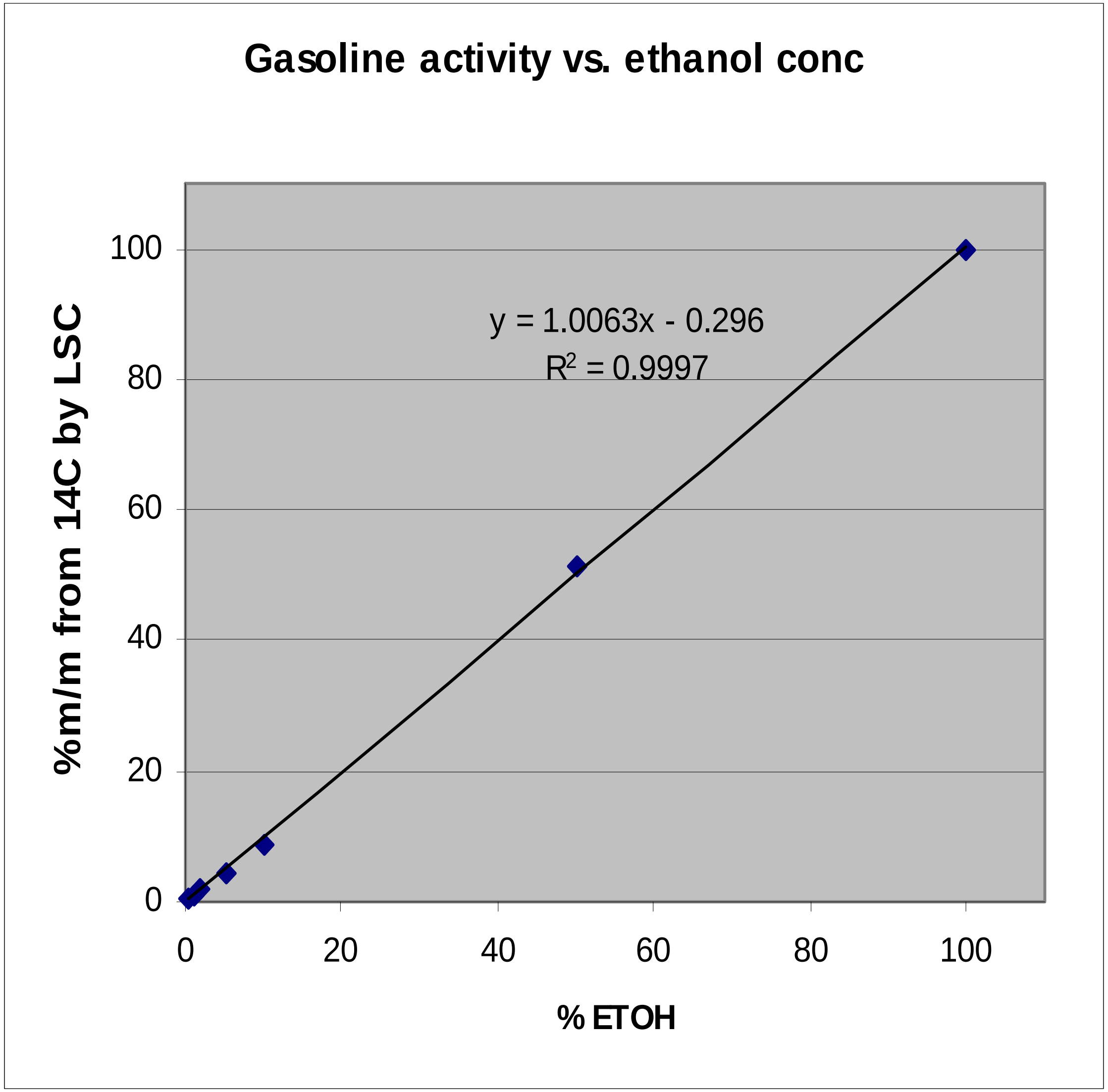
Spectrum end points reflect chemical quench levels of samples



Biofuel Analysis using LSC

- **Measured bioethanol concentration vs. the actual concentration by LSC (Quantulus) 0.5, 1, 2, 5, 10, 50 and 100 % EtOH**
- **10 mL sample mixed with 10 mL OptiScint HiSafe**

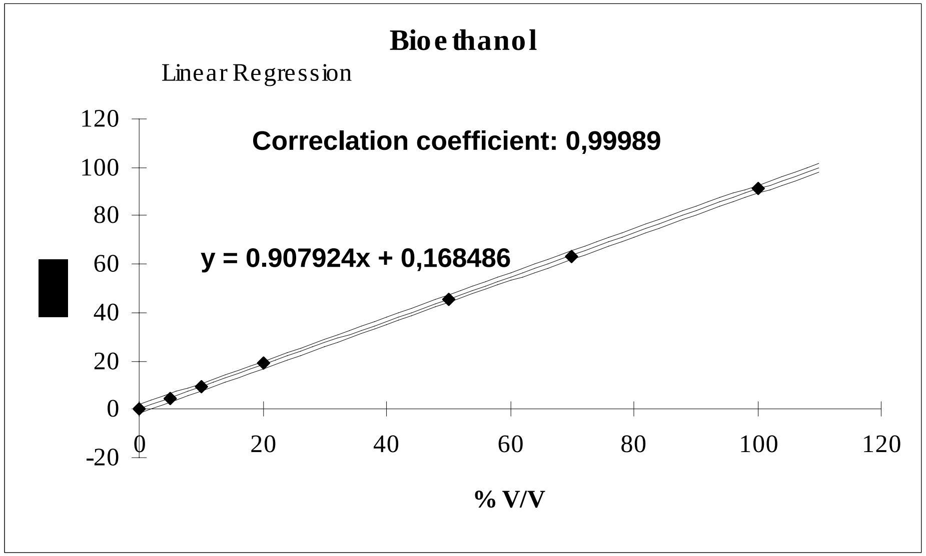


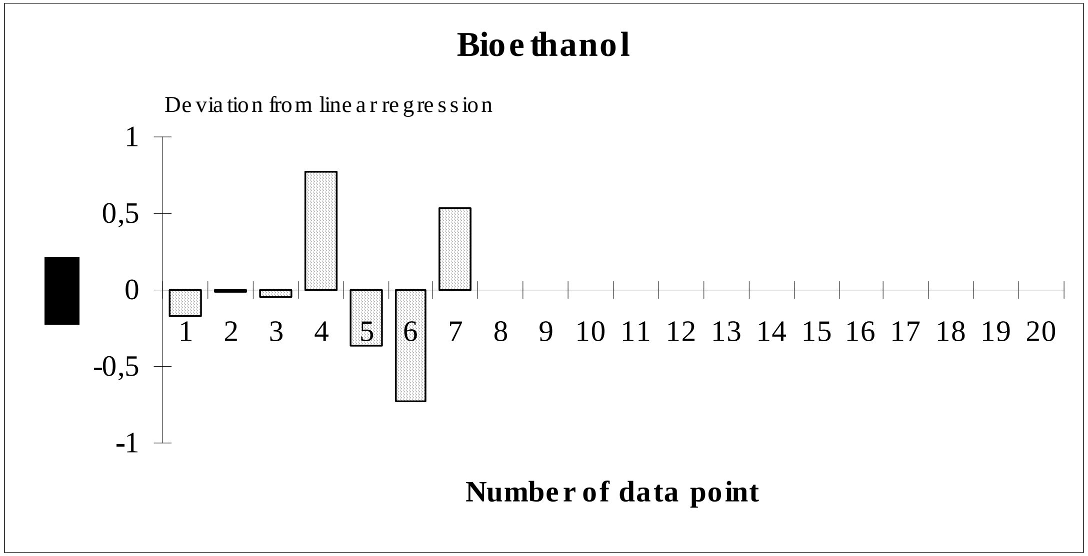


Further details: Ivo J. Dijs, E. van der Windt, L. Kaihola, K. van der Borg; Radiocarbon 48, 315-323 (2006)

Biofuel Analysis using LSC

- Measured bioethanol concentration vs. the actual concentration by LSC (TriCarb 3170) from 5, 10, 20, 50, 70 and 100 % EtOH.
- 10 mL sample mixed with 10 mL Ultima Gold F
- Samples need dark adaptation overnight
- Detection limit determined as 1.6 Bq/L following DIN 25482 part 1 in 8 hrs sample counting time, 2hrs background counting time (0.81 Bq/L if background counting time will be increased to 8 hrs) Equivalent to 0.5 – 1 DPM/sample
- Relative standard deviation of the method 1.7%





Ref.: M. Sagaischek, R. Edler

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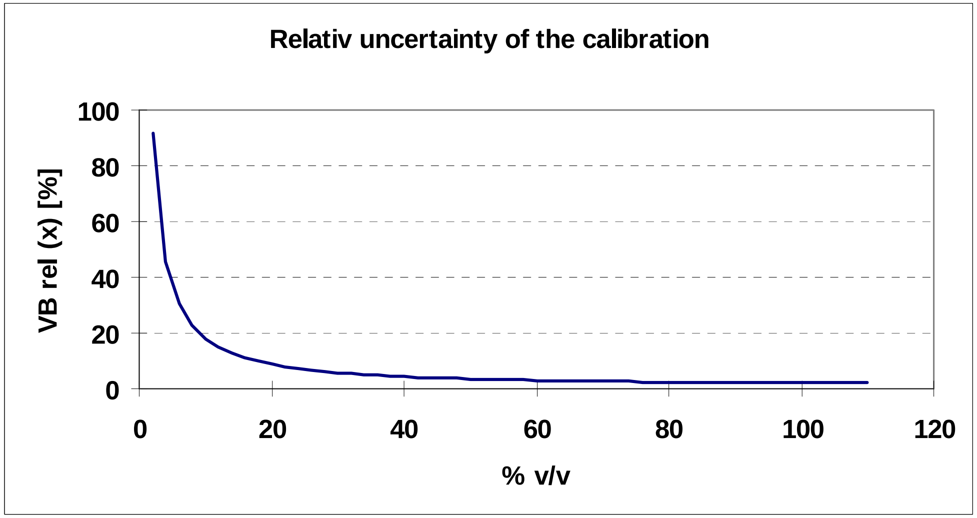
Biofuel Analysis using LSC

- **Austrian Detection limits are different and determined using DIN 32645. Method valid for concentrations of 5% Bioethanol or more.**
- **Increasing the counting time for the background sample can further increase the sensitivity.**



Bestimmungsgrenze = lowest amount that can be quantified with acceptable accuracy, determined using DIN 32645 approx. 5% v/v

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Types of Biofuel

Diesel :

- FAME - Fatty Acid Methyl Ester (in most cases yellow colour)
- RME – Rape Seed Methyl Ester (in most cases yellow colour)
- NExBTL - Next generation biomass to liquid
- GTL-products (gas to liquid, various technologies)

Gasoline :

- Bioethanol (colourless)
- ETBE, TAEE (colourless)
- Biogas

Types of Biofuel

Bioethanol (mainly Sweden) and ETBE (most European countries) can be analyzed without problems. Samples are colourless. Chemical quench is mainly depending on the amount of biogenic material but can easily be corrected using quench curves.

Mixtures of fossile fuel with Ethanol show strong chemiluminescence after exposure to daylight. Dark adaptation over night completely eliminates any luminescence.

As long as fuels do not contain much more than 5% biodiesel the dilution of the coloured material is efficient enough to prevent a significant influence on the accuracy of results.

Samples with higher amounts of coloured material can cause significant colour quench.

Bleaching of biodiesel samples was not very successful so far.
Oxidation is critical because samples tend to explode.
Addition of bromine helped to some extent.

Measurement of $^{14}CO_2$ from combustion of waste

As a result of the Kyoto protocol the European community agreed in a reduction of the CO_2 emission from fossil sources.

CO_2 emissions from biogenic sources are not included.

CO2 trading is necessary for countries emitting more CO2 than allowed.

As a result there is big interest in the determination of the CO2 resulting from combustion of biogenic sources.

Very interesting for all waste disposal companies combusting large amount of waste. Also large interest from concrete companies producing CaO from $CaCO_3$. This process already releases large amounts of fossil CO_2. However, the energy for this process comes partly from biogenic sources.

Measurement of $^{14}CO_2$ from combustion of waste

Currently contacts to a few concrete companies and the VÖEB (Vereinigung Öserreichischer Ensorgungsbetriebe).

Problem:

1. Customers again without experience in LSC technology.
2. Benzene synthesis seems to be too complex for inexperienced users.
3. Absorption of CO_2 in Carbo-Sorb E or other absorbing agents is not very efficient and reduces sensitivity.

Measurement of $^{14}CO_2$ from combustion of waste

Maximum uptake capacity of Carbo Sorb E is approx. 48 mmol CO_2 in in 10 ml of Carb Sorb, which is the maximum amount in a 20 ml vial.

48 mmol CO_2 is equal to 0.576 g carbon which is equal to 8.42 DPM/vial *) if we measure a sample with natural radioactivity.

Waste disposal companies and concrete companies in most cases use between 10 and 40% of biogenic material. Activities as low as 0.8 DPM/vial should result.

It should be possible to analyze most samples via CO_2 absorption in Carbo-Sorb E with long counting times.

Samples with significantly lower amount of biogenic CO_2 than 10% might need enrichment via benzene synthesis.

***) J. E. Noakes, G. Norton, R. Culp, M. Nigam, D. Dvoracek; LSC 2005, Advances in Liquid Scintillation Spectrometry, Proceedings of the 2005 International Liquid Scintillation Conference, Katowice, Poland, Edited by S. Chalupnik, F. Schönhofer, J. Noakes; page 259 (2007)**

Any suggestions?

If you have any suggestions for sample preparation to eliminate colour quench in biodiesel samples please let me know.

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