

Differentiation between fossil and biofuels by liquid scintillation beta spectrometry – direct method.

Abstract

Liquid scintillation spectrometry of ^{14}C in gasoline/ethanol and diesel oil was carried out using Quantulus™ and straight mixtures of fuel and an organic scintillation cocktail.

A linear correlation was found between the concentration of carbon that originates from the bioethanol (biocarbon) and the fuel mixture's ^{14}C activity in the range 0 – 100 % (m/m) bioethanol content. Because of the good linear correlations, quantitative determination of a fuel's biocarbon content can be made by ^{14}C analysis.

The direct method is also applicable to analysis of the biobased materials dissolvable in solvents, which can be mixed with scintillation cocktails.

Introduction

The world economy is strongly dependent on fossil fuels. Rising fuel prices and the Kyoto Protocol are driving a shift towards renewable energy sources to reduce CO_2 emissions.

The United States has declared a preference for using biobased materials in the U.S. Department of Agriculture program called the Federal Biobased Products Preferred Procurement Program (FB4P) [1]. Biofuel production is increasing in the U.S. to expand renewable energy usage and the Federal Government is pushing strongly towards an economy less dependent on fossil fuels.

Directive 2003/30/EC of the European parliament and of the council of 8 May 2003 on the promotion of the use of biofuels or other renewable fuels for transport, call for 5.75 % biofuel proportion from the total sales in EU by 2010 (traffic fuels, gasoline and diesel) [2].



Tax incentives have been introduced in many countries to promote biofuels. There is a growing interest in a method to differentiate between biofuels and fossil fuels, and to determine the content of biological components in fuel.

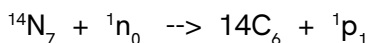
Since ^{14}C has decayed in fossil fuels, but is present in biofuels, liquid scintillation beta counting is suitable for characterization of the biofuel component. Biogenic components have been successfully analyzed in the case of food ingredients, wine, liquors and of course in archeological samples [3-7]. The oil industry, however, has so far used ^{14}C analysis mainly in process research.

ASTM standard D6866-06 lists three radioanalytical methods for analysis of biobased content of natural range materials, two of which make use of liquid scintillation spectrometry [8].

Direct LSC counting of fuel/cocktail mixtures is missing in the ASTM standard, which is not fuel specific. In this application note we describe ^{14}C radionuclide analysis with direct liquid scintillation counting [9].

^{14}C in nature

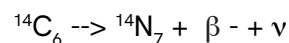
Cosmic radiation produces ^{14}C ('radiocarbon') in the stratosphere by neutron bombardment of nitrogen



The ^{14}C production rate is 7.5 kg/y. The ^{14}C concentration stays approximately constant due to rapid mixing of the atmosphere, although the cosmic intensity is higher at the poles due to the deflection of charged cosmic particles along the magnetic field lines of the earth (corresponding to neutron intensities in the ratio 5:1 at the poles and the equator, respectively). Consequently, ^{14}C atoms combine to form 'heavy' $^{14}\text{CO}_2$, which, except in the radioactive decay (and isotopic fractionation effects), is indistinguishable from the ordinary carbon dioxide. The total amount of ^{14}C on earth in equilibrium is 62 tons, which is 10^{-10} percent of all carbon in biosphere, atmosphere and oceans.

CO_2 concentration will be homogeneous over the globe and because it is used by plants, it will be uniformly present in all biosphere but has decayed in fossil materials due to its short half-life of 5730 years.

^{14}C decays by beta particle emission, where the simultaneously emitted neutrino shares the decay energy and therefore the beta particle is not monoenergetic, but has a long tailed energy spectrum with maximum energy 156 keV



Standard analysis methods for determining biobased content of carbon in biobased products

As mentioned previously, ASTM standard D6866-06 lists three radioanalytical methods for analysis of biobased content, two of which make use of liquid scintillation spectrometry [8].

Method A

ASTM Standard D6866-06 Ch 7.1 describes Method A in detail, which is based on trapping of CO_2 from a combusted sample into Carbo-Sorb®/methanol mixture. ULTIMA™ Gold is mentioned in the method as the cocktail.

We recommend Carbo-Sorb E (6013721) that can accept up to 4.8 mmol CO_2 per mL, and Permafluor® E+ (6013181) in ratios 1:1 or lower [10].

The carbon dioxide absorption method has also been used in radiocarbon dating [11-12].

Note: burning of fuel cannot be done in an ordinary oxidizer due to risk of explosion (use Parr oxygen combustion apparatus instead or catalytic incineration).

Method B

Method B is based on accelerator mass spectrometry (AMS) and isotope ratio mass spectrometry (IRMS) with an approach similar to the one used in routine radiocarbon dating. CO_2 is converted to graphite and ^{14}C atoms counted without waiting for the radioactive decay [9, 13].

Method C

Benzene synthesis is a routine sample preparation method in ^{14}C dating by LSC of archaeological samples [7, 13, 14]. 15 mg butyl-PBD powder is added as the primary solvent per mL benzene for sample counting in LSC systems such as the Quantulus, Revvity's ultra low-level liquid scintillation

spectrometer [9]. Glass or PTFE vials are needed to minimize loss of benzene. As no cocktail in liquid form is needed, the vial will contain a maximum amount of carbeneous sample.

Noakes *et al.* have reported measurements of biobased products using these ASTM standard methods [13].

Although methods A and C are less sensitive than that of using AMS/IRMS, they have two distinct advantages: 1) lower costs per evaluation and 2) much higher instrument availability worldwide. Sophisticated sample preparation methods are contained in methods B and C.

Direct ^{14}C analysis in fuels by liquid scintillation beta spectrometry

Method D – mix fuel sample directly with cocktail

This method is not presented in the ASTM Standard D6866-06.

Liquid scintillation counting allows direct detection of sample ^{14}C signal in cases where the sample can be homogeneously mixed with a cocktail. This is possible with most liquid samples, and a wide variety of cocktails are available, which accept organic and aqueous samples [15]. Counting efficiencies may vary due to variable quench effects introduced by the sample. Either quench calibration curves need to be made prior to the measurement, or radioactive standard material needs to be dissolved in the sample to enable later efficiency evaluation.

Organic cocktails accept a wide range of gasoline/ethanol mixtures and biodiesel.

Experimental

Liquid scintillation counting was performed at the Revvity Low Level Laboratory in Turku, Finland, using a Quantulus ultra low-level liquid scintillation spectrometer [9]. The temperature of the instrument and the samples were 18 °C. Vials were PTFE coated polyethylene vials with aluminum coated gaskets in the caps to ensure minimal sample loss during counting.

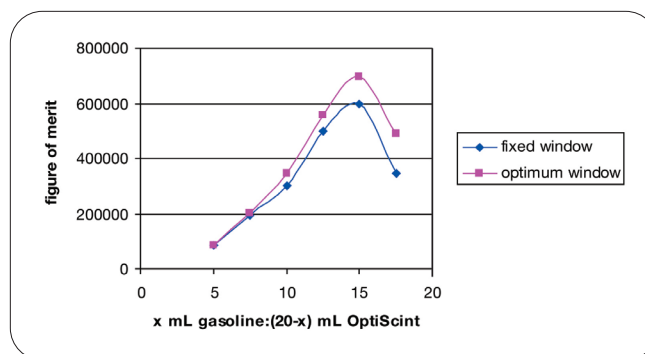


Figure 1: Figure of merit (EV)²/B for gasoline sample in OptiScint HiSafe as a function of sample volume in a plastic vial. The test was made with Quantulus #2200131 in Revvity Low Level Laboratory.

The cocktail used in the work was OptiPhase HiSafe2 (1200-436). Betaplate Scint (1205-440) and ULTIMA Gold F (6013179) are equivalent cocktails and accept 5 to 15 mL fuel per 15 to 5 mL cocktail. The best figures of merit (EV)²/B for pure gasoline are achieved at 14 mL fuel to 6 mL cocktail in a spectrum window extending to the spectrum endpoint. The background reduces at the high mixing ratios, compensating for the lower counting efficiency (Fig. 1). In ethanol, the point is at 12.5 mL. The inverse square root of the figure of merit is proportional to the minimum detectable concentration of activity in the sample. The figure of merit should be tested in each experimental setup, as the background level depends on the local environmental conditions and on the type of liquid scintillation counter. Also, the color of the fuel will have an effect on the figure of merit.

In this work, 10 mL fuel was mixed with 10 mL of sample due to the limited sample volume for the experiments.

Fuel samples were blended oxygenate-free unleaded gasoline (ULG95), bioethanol and fossil ethanol in the mass ratios as specified in Table 1. Also the carbon fraction and concentrations are given, which were derived from the applied quantities of blend components, the purity and the average molecular formula of the blend components, and the sample density [9].

An average molecular formula of $\text{C}_{6.53}\text{H}_{11.53}$ (89.89 g/mole) was derived from ^1H -NMR and ^{13}C -NMR (using 1,4-dioxane as the internal standard, 10% m/m) and GC-MS analysis [9].

Table 1: Composition of fuel mixtures and ^{14}C LSC analysis, 5.5 h counting.

Sample	Bio-ethanol (% m/m)	Fossil ethanol (% m/m)	ULG95 (% m/m)	Biocarbon content (mol/L)	Net activity and counting error		
					(Bq/l)	Err.	Err. (%)
1	0	0	100	0	0	0.1	-
2	100	100	0	34.39	100.6	0.8	0.8
3	0	0	0	0	0	0.1	-
4	0	10.64	89.36	0	0	0.1	-
5	10.01	0	89.99	3.29	9.32	0.3	2.7
6	5.18	0	94.82	1.7	4.9	0.2	3.8
7	1.99	0	98.01	0.65	1.91	0.2	4.7
8	1.02	0	98.98	0.33	1.08	0.2	5.3
9	0.55	0	99.45	0.18	0.79	0.2	5.5
10	50.21	49.79	0	17.26	51.7	0.6	1.1
11	98.05	1.95	0	33.72	99.2	0.9	0.9
12	99.01	0.99	0	34.05	99.9	0.9	0.9
13	99.5	0.5	0	34.22	100.4	0.9	0.9

^{14}C Analysis

The fuel samples (10 mL) were combined with OptiPhase HiSafe2 (10 mL) and analyzed for 5.5 hours.

A spectrum window starting from Ch 125 was applied to exclude a contribution from chemiluminescence, which was observed with the gasoline-ethanol mixtures only. High bias can also be used in discrimination of chemiluminescence with Quantulus. To determine counting efficiencies, the initial measurements were followed by internal standardization, i.e. adding 100 μl fossil gasoline containing 2090 DPM of $[4-^{14}\text{C}]$ -cholesterol (product number 1210-122) to each sample. Total counting time of 5.5 hours was composed of cycles of 30 minutes each, allowing statistical verification of sample stability during counting. Background samples had no ^{14}C activity, i.e. they were either fossil fuel samples or synthetic ethanol.

Results and discussion

A fuel's ^{14}C activity is a direct measure of its biocarbon concentration (or the carbon fraction with a biological origin). ^{14}C analysis of a fuel sample of unknown composition thus provides the concentration of biocarbon originating from the biofuels components, which may be different from the amount of biofuel in the total fuel mixture.

The carbon content of a fuel can be derived from standard compositional analysis and density measurements. Bioethanol is considered in the present work to be representative for all kinds of biofuels containing carbon.

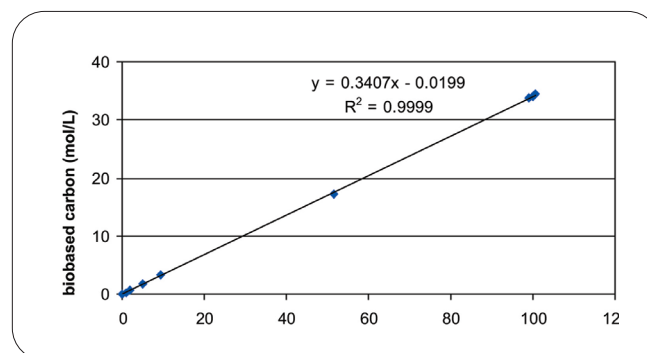


Figure 2: Relationship between observed biobased ^{14}C concentration.

^{14}C analysis of gasoline-ethanol mixtures by LSC

The ^{14}C activity of each gasoline-ethanol mixture was measured by LSC (Table 1). For fossil fuel samples with a small content of bioethanol, the error percentages in ^{14}C activity are higher than for bioethanol samples with a small quantity of fossil ethanol. Nonetheless, errors in ^{14}C activity

per liter clearly remain below 10% at a counting time of 5.5 hours per sample. A further reduction could be achieved by longer counting periods; error reductions of 29 and 60 percent were achieved by counting for 11 and 34 hours, respectively. Hence, the error reduction is inversely proportional to the square root of counting time.

The concentration of biocarbon ($[C_b]$) in samples 1-13 was calculated by using sample composition and density. $[C_b]$ was plotted against ^{14}C activity and a linear least squares fit gave an excellent correlation (Fig. 2.). A calibration plot of $[C_b]$ versus sample activity per unit volume is sufficient for determination of the biocarbon concentration.

When the molecular formula of the biofuel component is known, the concentration of a biofuel component in the fuel mixture can be calculated from the concentration of biocarbon that is derived from the ^{14}C measurement. In the case that several biofuels types form the total fuel mixture, separation of the biofuel components may be required prior to individual ^{14}C analysis.

Hence, instead of expressing the biofuel content by its mass or volume fraction of the fuel mixture it would be more convenient to use 'biocarbon content'.

The specific ^{14}C activity for carbon is higher in 2005 than in 1950 because of atmospheric atomic bomb testing after 1950. A treaty in 1963 stopped these tests and a decrease in the specific ^{14}C activity level resulted. The specific ^{14}C activity of carbon was about 17.80 DPM/g in 1980, 15.75 DPM/g in 1990, and 14.78 DPM/g in 2000. The reference level in 1950 was 13.56 DPM/g. Hence, the variation in specific ^{14}C activity for carbon over the last decades affects the precision in the determination of the biocarbon content.

Comparison of direct method to methods A through C

Direct biofuels measurement has clear advantages over the methods presented in the ASTM Standard D6866-06. Cost, sensitivity and speed are in favor of the direct liquid scintillation counting method (Tables 2 and 3). Color in direct liquid scintillation is problematic and its removal not straightforward. As neither oxidization nor benzene synthesis are required, the method is suitable to laboratories with normal facilities and personnel trained for routine LSC.

Table 2: Merits and drawbacks of the proposed ^{14}C fuel analysis methods.

Method	Merit	Drawback
Method A: CO ₂ & LSC	Less sample preparation than in Method C, lower costs per evaluation, good 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 ₆ H ₆ & LSC	High sensitivity, precise, good instrument availability worldwide	Slow sample prep, small capacity, new synthesizers hard to acquire, benzene is carcinogenic
Method D: Direct LSC Analysis	Minimal, fast sample preparation Good sensitivity Lower costs per evaluation Good 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. Color in fuel samples need to be removed

Table 3: Comparison of methods for ¹⁴C based analysis (Method A through C analysis is based on Noakes et al. Tables 2 and 3 [13]).

Method	Sample preparation time hr	Analysis time min	Analysis cost** (USD)	Instrument \$(000)	Sample size g	Contamination risk***	Precision %
Method A* Liquid Scintillation Counting with CO ₂ trapping	3	1300	250	150	0.2-1	Moderate	< 9
Method B* Accelerator Mass Spectrometry (AMS)	2	20	400	2000	0.001	High	< 1
Method C* Liquid Scintillation Counting with Benzene Synthesis	3	1300	250	150	2-10	Low	< 2
Method D Direct Liquid Scintillation Analysis	0.1	360	150	100	5-10	Low	< 6

* ASTM Standard method for biobased materials analyses

** Includes the depreciation of equipment

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

Conclusion

¹⁴C analysis of mixtures of bioethanol, fossil gasoline and fossil ethanol by LSC showed that the fraction of carbon that originates from biofuel components (biocarbon fraction) can be determined quantitatively. AMS and LSC results were well correlated [9].

The production date of the biobased fuel needs to be known. Older fuel would have higher ¹⁴C than the one produced of fresh biogenic material.

Direct mixing of sample and cocktail allows larger sample volumes and radioactivity in vials than CO₂ absorption method. It also allows usage of PTFE coated plastic and non-radioactive vials, which cannot be used in CO₂ method (and benzene counting).

Direct ¹⁴C analysis of biobased materials, plastics for instance, which are dissolvable in aromatic solvents, is analogous to the analysis of biofuels presented in this note.

For more information about this or other liquid scintillation applications or Quantulus, please contact Revvity at 1-800-762-4000 toll free in the U.S. and Canada or at 1-203-925-4602 outside of the U.S.

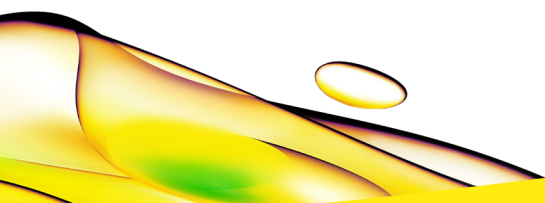
Acknowledgements

Fuel samples were provided by Kuwait Petroleum Research & Technology b.v., P.O. Box 545, NL-3190 AL Hoogvliet, the Netherlands for a joint ¹⁴C analysis project.

References

1. US Department of Agriculture has a program called Federal Biobased Products Preferred Procurement Program (FB4P), 7 CFR 2902, Designation of Biobased Items for Federal Procurement <http://www.biobased.oce.usda.gov/files/03-31347.pdf>
2. Baxter, M.S. and Walton, A., Carbon-14 Concentrations in Recent Wines and Spirits. 1971. J. Food Sci. 36: 540.
3. Martin G.E., Noakes J.E., Alfonso F.C., Figert, D.M. 1981. Liquid Scintillation Counting of Carbon-14 for Differentiation of Synthetic Ethanol from Ethanol of Fermentation. Journal of the Association of Official Analytical Chemists. 64:1142-1144.
4. McWeeny D.J., Bates M.L. 1980. Discrimination Between Synthetic and Natural Ethyl Alcohol in Spirits and Fortified Wines. Journal of Food Technology. 15:407-412.

5. Schönhofer, F. 1989. Determination of ^{14}C in Alcoholic Beverages. *Radiocarbon* 31(3):777-784.
6. Gupta, S.K. and Polach, H.A., *Radiocarbon Dating Practices at ANU. Handbook. Radiocarbon Laboratory, Research School of Pacific Studies, Australian National University, Canberra, 1985.*
7. American Society for Testing and Materials [ASTM]. Vol. 8.03. Method D6866-06. Standard Test Methods for Determining the Biobased Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis, 2006, www.astm.org.
8. Dijs, Ivo J., van der Windt, Eric, Kaihola, Lauri and van der Borg, Klaas. 2006. Quantitative Determination by ^{14}C Analysis of the Biological Component in Fuels. *Radiocarbon*, 48(3): 315-323.
9. Thomson, J. and Burns, D.A., Radio-Carbon ($^{14}\text{CO}_2$) Trapping and counting, Application Note CS-001, Revvity LAS (updated May 2005 by R. Edler).
10. Aravena, R., Drimmie, R.R., Qureshi, R.M., McNeely, R. and Fabris, S. 1989. New Possibilities for ^{14}C Measurements by Liquid Scintillation Counting, *Radiocarbon* 31, 387-392.
11. Qureshi, R.M., Aravena, R., Fritz, P. and Drimmie, R.R. 1989. The CO_2 absorption method as an alternative to benzene synthesis method for C14 dating. *Appl. Geochem.* 4, 625-633.
12. Noakes J.E., Norton G., Culp R., Nigam M., Dvoracek D. 2007. A comparison of Analytical Methods for the Certification of Biobased Products. LSC2005, *Advances in Liquid Scintillation Spectrometry. Radiocarbon* 49: 259-272.
13. Higham, T. Radiocarbon WEB-info. URL: <http://www.c14dating.com>.



revvity