



# Analysis of fuel using the Direct LSC method determination of bio-originated fuel in the presence of quenching



Charles G. Doll\*, Cherylyn W. Wright, Shannon M. Morley, Bob W. Wright

Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA

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## ABSTRACT

A modified version of the Direct LSC method to correct for quenching effect was investigated for the determination of bio-originated fuel content in fuel samples produced from multiple biological starting materials. The modified method was found to be accurate in determining the percent bio-originated fuel to within 5% of the actual value for samples with quenching effects  $\leq 43\%$ . Analysis of highly quenched samples was possible when diluted with the exception of one sample with a 100% quenching effect.

## 1. Introduction

Introduction of federal tax subsidies for bio-originated fuels has created the potential of representing fossil fuel as counterfeit bio-based fuel in order to illegitimately collect subsidies or tax credits. For example, renewable diesel created from hydrotreating (refinery based hydrogenation) fats and oils to remove metals, oxygen, and nitrogen become similar to petroleum-based diesel and meet the same specifications. To thwart the counterfeiting of bio-originated fuels, methods to determine the presence or absence of bio-originated fuel in a sample are of interest. The absence of  $^{14}\text{C}$  in fossil fuel due to decay creates a signature that can be exploited by Liquid Scintillation Counting (LSC) for determination of bio-originated fuel in a mixed sample. Therefore, LSC can provide a simple method of evaluating bio-originated fuel content. The Direct LSC method has been outlined in studies for the determination of bio-originated fuel composition (Elmer, 2009; Dijks et al., 2006; Kristof and Logar, 2013; Kristof et al., 2014; Idoeta et al., 2014; Norton et al., 2012; Norton and Woodruff, 2012) and was investigated as a method of distinguishing bio-originated fuel and petroleum based fuels.

While the Direct LSC method has promise as a simple method to distinguish between bio-originated and petroleum based fuels, quenching effects create a problem for some samples resulting in lower LSC efficiency relative to unquenched samples. This quenching is a result of either chemical or color interference in the solution that reduces the light emitted from the LSC cocktail (Minne et al., 2009; Kristof et al., 2011; Pawlyta et al., 1998; Varlam et al., 2001). To allow for the analysis of quenched samples, a method to analyze and correct for

quenching in diverse fuel samples is required. We have developed a Modified Direct LSC method which incorporates internal spiking along with sample preparation techniques for the determination of the percent bio-originated fuel content in samples which exhibit varying amounts of quenching.

## 2. Experimental

### 2.1. Materials

Chemicals used in this study were: toluene obtained from Fisher Scientific, Ultima Gold F liquid scintillation cocktail obtained from Perkin Elmer and a  $^{14}\text{C}$ -n-hexadecane certified standard with a specific activity of  $5.402 \times 10^4 \text{ Bq/g}$  purchased from National Institute of Standards and Technology. In addition, Glass pipettes and 20 mL glass LSC vials with foil lids were used for all sample analysis to avoid any potential leaching of organics from plastic into the fuel. Fuel samples used in this study are listed in Table 1 and Table 2. The “Bio” samples of Table 2 are biodiesels that were determined to have less than approximately 0.1% diesel blending by gas chromatography (GC/FID) analysis; they all meet ASTM D6751 requirements for Grade No. 1-B or Grade No. 2-B biodiesel for parameters tested. The “Renewable” samples of Table 2 are homogeneous hydrocarbon oils as determined by gas chromatography/mass spectrometry (GC/MS) analysis; they both meet ASTM D975 requirements for No. 2-D diesel fuel oil for parameters tested.

\* Corresponding author.

E-mail address: [charles.doll@pnnl.gov](mailto:charles.doll@pnnl.gov) (C.G. Doll).

**Table 1**  
Fuels used for standard curve.

Sample name	Composition	Starting material	Description
Renewable Blend 1	Bio-originated fuel blend of Renewable fuel from two sources	Renewable feedstock originating from biological sources	Renewable that meets ASTM D975 requirements for Grade No. 2-D diesel fuel oil for parameters tested
Fossil 1	Petroleum Diesel	Diesel fuel from Chevron Phillips Chemical Company, LP, SRF High Cetane Check Fuel Lot 2BPCFH01	Used for Standards
Fossil 2	Petroleum Diesel	DF21502 Diesel fuel received as part of ASTM Proficiency Testing Program	Used for Sample Dilution

## 2.2. LSC analyses

Sample analysis was performed on a Perkin Elmer Quantulus 1220 Low Level Liquid Scintillation Spectrometer. The instrument parameters were set to 60 or 300 min counting time,  $^{14}\text{C}$  high energy configuration, high coincidence bias, PAC setting of 1 and channel window of 50–650.

## 2.3. Spiking solution preparation

Serial dilution of the  $^{14}\text{C}$ -n-hexadecane standard in toluene was performed to prepare a 2.5 dpm/ $\mu\text{L}$  spiking standard solution.

## 2.4. Standard and sample preparation

Standards were prepared by mixing weighted aliquots of 100% bio-originated fuel (Renewable Blend 1) and 100% fossil fuel (Fossil 2) in glass LSC vials for a total of 8 mL. Fuels used for preparation of the standard curve are listed in Table 1. Prior to analysis, 12 mL of Ultima Gold F was added to each vial. For the standard curve, unspiked standards containing 0%, 3.8%, 8.8%, 12.5%, 16.3%, 21.3%, 25.0%, 37.5%, 50.0%, and 100.0% bio-originated fuel were prepared. After counting these unspiked standards, spiked standards were prepared and counted by adding 40  $\mu\text{L}$  of the 2.5 dpm/ $\mu\text{L}$  spiking standard solution (~100 dpm total spike) to each vial.

Samples were prepared in the same manner as for the standard curve with 8 mL of 100% or diluted bio-originated fuel – fossil fuel was used to dilute sample when preparing 10% and 20% bio-originated fuel samples. Spiked samples were prepared in the same manner as the spiked standards.

## 2.5. Sample cleanup

Sample cleanup of highly quenched and dyed bio-originated fuel was achieved by passing the sample through a Carbon/ $\text{NH}_2$  solid phase extraction (SPE) tubes (Mega BE, Agilent Technologies) using a plunger at approximately 4 mL/min. The fuel was added to a fresh SPE tube in

**Table 2**  
Samples analyzed.

Sample	Composition	Starting material <sup>a</sup>	Color
Bio 1	100% Bio-originated fuel	Unknown	Light amber
Bio 2	100% Bio-originated fuel	Soy or other vegetable based oil*	Pale yellow
Bio 3	100% Bio-originated fuel	Beef tallow	Deep yellow
Bio 4	100% Bio-originated fuel	Soy or other vegetable based oil*	Clear
Bio 5	100% Bio-originated fuel	Soy or other vegetable based oil*	Pale yellow
Bio 6	100% Bio-originated fuel	Animal based fat*	Very pale yellow
Bio 7	100% Bio-originated fuel	Corn oil	Deep orange
Bio 8	100% Bio-originated fuel	Camelina oil	Yellow
Bio 9	100% Bio-originated fuel	Palm heart oil	Yellow
Bio 10	100% Bio-originated fuel	Soy or other vegetable based oil*	Brownish amber
Bio 11	100% Bio-originated fuel	Soy or other vegetable based oil*	Deep yellow
Renewable 1	100% Renewable Fuel	Renewable feedstock originating from biological sources	Clear
Renewable 2	100% Renewable Fuel	Renewable feedstock originating from biological sources	Clear

<sup>a</sup> Starting materials marked with an \* are based on GC/FID analysis; others are based on information provided with the sample.

4-mL increments. To avoid sample dilution, no eluent was used. The sample was analyzed by GC/FID prior to and after cleanup.

## 2.6. Determination of counting efficiency and percent bio-originated fuel

By comparing the expected contribution of the spiking solution to the actual difference between spiked and unspiked samples, the percent quenching for each sample was determined along with the quenching factor.

$$\% \text{ Quenching} = 100 - \frac{\text{SpikedCPM} - \text{UnspikedCPM}}{\text{ExpectedCPM}}$$

$$\text{Quenching Factor} = (100 - \% \text{ Quenching}) \times 100$$

After correcting for background, this was used to calculate a quench corrected CPM values for each sample:

$$\text{Quench Corrected CPM} = \frac{\text{CPM}}{\text{Quenching Factor}}$$

Samples were efficiency corrected and compared to standard curve to determine the percent bio-originated fuel in the unknown sample.

## 3. Results and discussion

### 3.1. Preparation of standard curve

A standard curve was prepared by mixing varying amounts of 100% bio-originated fuel and petroleum fuel which were uncolored to avoid quenching effects. This series of samples contained 0%, 3.8%, 8.8%, 12.5%, 16.3%, 21.3%, 25.0%, 37.5%, 50.0%, and 100.0% bio-originated fuel. The fuels used for the standard curve and samples are listed in Table 1. After the initial analysis by LSC the standards were spiked with a  $^{14}\text{C}$  internal standard and reanalyzed to correct for any potential quenching effects.

### 3.2. Determination of standard stability and optimal LSC counting

The standard curve samples were stored at room temperature in the

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