



## Comparison of radiocarbon techniques for the assessment of biobase content in fuels



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### ABSTRACT

A comparison was made between various radiocarbon measurement techniques for the purpose of quantifying each methods capability for the proper apportionment of biobase-derived additives to gasoline. Measurement techniques include (1) direct liquid scintillation counting, (2) carbon dioxide absorption followed by liquid scintillation counting, (3) conversion to benzene followed by liquid scintillation counting and (4) accelerator mass spectrometry. In addition, stable isotope ratios of carbon and hydrogen were determined to assist in the authentication of a fuels source with regard to petrochemical or biobase origin is required for the confirmation of minimum anti-knock components, consumer awareness and proper assessment for regulatory taxation. Accelerator mass spectrometry was found to be the most precise technique followed by conversion of fuel to benzene with liquid scintillation counting and direct counting by liquid scintillation counting. Finally, liquid scintillation counting of absorbed carbon dioxide was found to be the least precise and should not be used for this analysis. The high to low precisions correlate with the high to low cost of equipment and support required by each of these methods except for direct liquid scintillation counting. Therefore, laboratories interested in developing capability to perform such authentication can use this data to consider the economics of the optimum technique to use for radiocarbon measurement.

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### 1. Introduction

In the United States, the 2007 Energy Independence and Security Act, mandates the use of 136 billion liters of renewable fuel by 2022. Nearly half, or 61 billion liters, of this requirement will be met by cellulosic biofuel alone. Currently, renewable ethanol satisfies this requirement in the form of E10 gasoline or approximately 10% ethanol, blended in nearly 90% of all gasoline sold in the United States. Higher ethanol additions up to 85% are increasing as new flex-fuel vehicles are introduced into the market.

To insure accuracy in blending ethanol and gasoline for the purpose of adherence to requirements and improved quality control, the University of Georgia's Center for Applied Isotope Studies provides biobase testing by ASTM method D6866-12 and stable isotope ratio analysis. Methods such as these have been used for nearly ten years to verify biobased additions to petrochemicals (Dijks et al. 2006; Edler 2009; Noakes et al. 2011; Standard Test Methods, 2012). Currently ASTM D6866-12 allows only LSC benzene method C or AMS method B for biobase determinations, eliminating the carbon dioxide absorption method A, a few years ago. Direct LSC counting has not been a part of the ASTM method. However, to

anticipate the growing need for biobase addition verification, and the possible future inclusion of other methods based on radiocarbon measurement, all four of these methods are compared in this study of various ethanol gasoline mixtures to assist suppliers, blenders and consumers to properly assess these ever changing products.

### 2. Methods

Nineteen gasoline samples containing advertised 0, 10 and 85% ethanol additions were collected from over fifteen locations in the State of Georgia. Eight of these were reported as ethanol free or 100% gasoline, 6 were E10 or 10% ethanol and 5 were reported as E85 or 85% ethanol added gasoline. Samples were collected in pre-rinsed glass containers with teflon-lined caps.

Isotopic composition including  $^{14}\text{C}$  and stable isotope ratios  $^{13}\text{C}/^{12}\text{C}$  and deuterium/hydrogen (D/H) were conducted using liquid scintillation counting, accelerator mass spectrometry and stable isotope ratio mass spectroscopy. Standard sample preparation techniques follow that used for stable isotope ratio analysis using high temperature combustion to carbon dioxide and water and high vacuum cryogenic sample isolation. Water was reduced to hydrogen gas over hot zinc prior to D/H measurement.

Three liquid scintillation methods were considered for biobase ethanol determination; benzene synthesis, carbon dioxide absorption

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in amine (Carbosorb) and direct counting (Permafluor-F), all measured in low-level liquid scintillation counters.

For benzene synthesis, adequate sample was combusted within a Parr combustion apparatus to produce 10 L of CO<sub>2</sub>. Nine liters was processed by traditional benzene synthesis to lithium carbide, hydrolyzed into acetylene and finally trimerized into benzene. Low potassium-40 glass 7 mL scintillation vials were used to contain 3 mL benzene produced from the sample along with 0.5 mL of standard scintillation cocktail composed of PPO and POPOP dissolved in benzene. The 0% ethanol gasoline, equivalent to 100% fossil fuel, was used as background determinants while oxalic acid SRM was used for efficiency calculations. Based on the addition of 85% modern carbon in the E85 ethanol/gasoline mixture, a computed <sup>14</sup>C activity could be used for “near-modern” activity levels and efficiency determinations as well as Oxalic acid SRM.

For the Carbosorb absorption method, one liter of CO<sub>2</sub>, left over from original Parr combustion, was transferred using liquid nitrogen to a 50 mL stainless steel bottle for forced absorption into 10 mL Carbosorb-E solution. Modification was made to the method of absorption detailed in Noakes et al. (2006), where a pressurized stainless steel bottle and forced absorption replaced the low-pressure apparatus and self-absorption of one liter of carbon dioxide into the pre-requisite 10 milliliters (mL) of Carbosorb. Using pressurized but controlled introduction of CO<sub>2</sub> into the 20 mL LS vial, while monitoring an overflow vial for indication of gas introduction rate, a high efficiency of absorption was achieved. As for benzene synthesis samples, CO<sub>2</sub> from 0% ethanol gasoline, equivalent to 100% fossil fuel, was used for background determination and E85 (85% ethanol) were proportioned relative to modern activity level was used for near-modern activity. Background and counting efficiency could then be computed.

For direct liquid scintillation counting, samples were prepared by adding 10 mL of fuel to 10 mL Permafluor-F cocktail in standard 20 mL glass LS vial. All samples exhibited a slight yellow tint but exhibited similar quench parameters and had no quench correction applied.

Oxalic acid standard reference material and spectrographic grade benzene (fossil-fuel derived) were likewise combusted and processed for efficiency and background determinations respectively, for comparison to 0% ethanol gasoline, equivalent to 100% fossil fuel and 85% ethanol/gasoline mixture, equivalent to near-modern activity.

A few mL of CO<sub>2</sub> from the original Parr combustion, was also collected for graphitization for AMS and for measurement in an isotope ratio mass spectrometer (IRMS) for isotope ratio determination using Thermo model 252, Delta XL and Delta V IRMS with ratios generated against NIST referenced gases and reported relative to V-PDB and V-SMOW international standards. Liquid scintillation <sup>14</sup>C determination made use of Packard model 1050 and Quantulus counters. AMS <sup>14</sup>C measurement was made using National Electrostatics Corporation (NEC) 500 and 250 kV accelerators.

### 3. Discussion

#### 3.1. Analytical data

Table 1, lists the radiocarbon data for the nineteen samples of blended fuels sampled. They are listed in increasing ethanol content from none added (E0) to 85% ethanol addition (E85). Brand names are included and NoBrand for stations that did not post the fuel supplier. <sup>14</sup>C is in dpm/gC and one standard deviation error derived from combined instrument precision and replicate analyses of the same sample. The first two columns are AMS data followed by liquid scintillation data by the three methods benzene synthesis, Permafluor direct counting and Carbosorb carbon dioxide absorption. A question mark is followed on three E0 samples, which were found to have

**Table 1**

<sup>14</sup>C activity (disintegrations per minute per gram carbon) by Brand and blend, by AMS and LSC Benzene (Ben), Permafluor F (Perm) and Carbosorb P+E (Carb) methods. SD represents one standard deviation.

Supplier/ Brand	Ethanol blend	<sup>14</sup> C AMS		<sup>14</sup> C LSC					
				Ben		Perm		Carb	
		<sup>14</sup> C	SD	<sup>14</sup> C	SD	<sup>14</sup> C	SD	<sup>14</sup> C	SD
Valero	E0	0.04	0.01	0.14	0.08	0.00	0.06	0.00	1.83
NoBrand	E0?	0.99	0.01	1.03	0.05	1.08	0.04	0.74	0.89
Pure	E0	0.05	0.01	0.11	0.06	0.01	0.06	1.53	1.40
Marathon	E0	0.03	0.01	0.17	0.09	0.02	0.04	0.59	1.86
Citgo	E0?	1.00	0.01	1.03	0.07	1.23	0.07	1.49	1.83
NoBrand	E0	0.04	0.01	0.10	0.07	0.00	0.06	0.80	0.44
Pure	E0?	0.88	0.01	0.88	0.05	1.02	0.06	1.81	0.24
NoBrand	E0	0.07	0.01	0.07	0.08	0.06	0.03	0.00	1.16
BP	E10	1.01	0.02	1.00	0.06	1.12	0.07	1.76	1.21
Marathon	E10	1.05	0.02	1.00	0.07	1.27	0.04	3.43	1.86
Exxon	E10	1.01	0.02	1.02	0.08	1.02	0.06	2.02	0.66
Citgo	E10	1.02	0.02	1.03	0.07	1.24	0.11	3.16	1.72
UGA	E10	1.03	0.02	1.02	0.07	1.17	0.06	2.58	1.31
Shell	E10	1.12	0.02	1.08	0.08	1.28	0.08	3.26	0.67
UGA	E85	11.05	0.13	10.63	0.11	10.42	0.09	9.30	1.73
Safa	E85	11.62	0.09	10.93	0.12	10.04	0.23	9.03	0.66
Citgo	E85	11.55	0.09	11.39	0.10	11.22	0.10	10.69	1.79
Chevron	E85	11.57	0.10	11.33	0.08	12.24	0.12	11.32	1.18
Exxon	E85	9.58	0.09	9.12	0.08	9.46	0.18	9.69	1.01

higher <sup>14</sup>C content than advertised. In other words these samples resembled E10 fuels rather than E0 fuels.

Table 2 lists the stable isotope ratio analyses, by brand and blend along with one standard deviation error based on replicate analyses of the same sample. The data presented here are referenced to the international standards for carbon and hydrogen V-PDB and V-SMOW, and are in standard nomenclature of parts per mil (‰). More negative numbers imply a depletion of the heavier isotope <sup>13</sup>C or deuterium, and more positive values indicate enrichment of the heavier isotope. The greater addition of corn-derived ethanol is apparent in the E85 fuels as corn is considerable enriched in the heavier <sup>13</sup>C, which results in the less negative values indicated here.

#### 3.2. LSC analysis

Most methods have given relatively comparable results but with significantly different standard deviations. Standard deviations are computed based on instrument precision but also on replicate analyses of the same sample. The later having the larger effect on error. As Fig. 1 portray, the LSC benzene method exhibited low standard deviations with a maximum of 0.12 dpm/gC. The permafluor direct counting was nearly as good with demonstrated maximum error of 0.23 dpm/gC. The correlation coefficient of 0.99815 indicates very good agreement between the benzene synthesis and direct counting methods by liquid scintillation counting. These are nearly as good as the demonstrated precision of the AMS data where the standard deviation only exceeds 0.1 dpm/gC for a single E85 sample. Comparison of AMS generated data to that from LSC benzene method in Fig. 2, shows very good agreement based on a correlation coefficient of 0.99946. Standard deviations for each sample, and the close correlation between different analytical methods shown here at least justify the inclusion of the two methods, benzene synthesis and AMS, in the ASTM D6866-12 method. Although surprisingly precise, <sup>14</sup>C by direct counting was less accurate when compared with the benzene <sup>14</sup>C measurement. Even using a Quantulus shielded counter, direct counting background activity was very high relative to benzene background activity. Although a good correlation exists, a larger error was seen for the 85% ethanol samples relative to benzene or AMS <sup>14</sup>C measurements.

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