



## Accurately Quantify Methanol and Ethanol in E85 Biofuel by D5501 with New Rtx<sup>®</sup>-DHA-150 Column

By Barry Burger <sup>a</sup>, Jaap de Zeeuw <sup>b</sup>, and Jan Pijpelink <sup>a</sup>

<sup>a</sup> Restek Corporation, 110 Benner Circle, Bellefonte, PA, US

<sup>b</sup> Restek Corporation, Weerhaan 9, Middelburg, The Netherlands

Restek Corporation, 110 Benner Circle, Bellefonte, PA, US [www.restek.com/petro](http://www.restek.com/petro)

Ethanol and methanol levels in biofuels must be accurately determined as they impact fuel performance and influence sales price. Since fuel ethanol must be denatured with gasoline to render it nonpotable prior to transport, analysis is complicated by the presence of gasoline hydrocarbons. Testing is usually done according to ASTM Method D5501, which recommends either a 100m or a 150m column. This method currently targets the determination of ethanol at 93-97% and methanol at 0.1-0.6%, based on mass percent in product; however, discussions have been initiated to expand the range to 20-99%. The main challenge in ASTM D5501 is getting clean elution of both ethanol and methanol, without the coelution of components from the gasoline denaturant. Coelution of methanol and isobutane is particularly problematic and may require time-consuming cryogenic conditions.

ASTM D5501 provides conditions for 100 meter and 150 meter columns, as a large number of theoretical plates are necessary to obtain adequate separations. Separations can be accomplished on 100 meter columns operated under cryogenic conditions, but this results in longer analysis times. Operating conditions for 150 meter columns do not require cryogenics, but the columns that have been available to the industry to date suffer from poor peak shape and extreme tailing of the methanol and ethanol peaks. Recently, a 30 meter column has been marketed for this application, but the ability to separate methanol and isobutane is questionable. A new 150 meter column, the Rtx<sup>®</sup>-DHA-150 column, has been developed by Restek, specifically for D5501 analysis.

The Rtx<sup>®</sup>-DHA-150 column is highly versatile and can be used for detailed hydrocarbon analysis (DHA) during process monitoring, in addition to ethanol/methanol quantification according to ASTM D5501. DHA applications are available at [www.restek.com/petro](http://www.restek.com/petro) and include the analysis of light fractions of natural gas, liquefied petroleum gas (LPG), and unleaded gasoline. Restek has collaborated heavily in the past with Neil Johansen (now retired), one of the original developers of DHA. Neil oversaw the evolution of DHA columns from the original 55 meter 100% polydimethylsiloxane polymer columns in borosilicate glass to the 100 meter modern fused silica columns with up to 500,000 theoretical plates. The long-term partnership with Neil was instrumental in the development of Restek's DHA and PONA columns, and the technological advances made there have been applied to this new column for fuel ethanol testing.

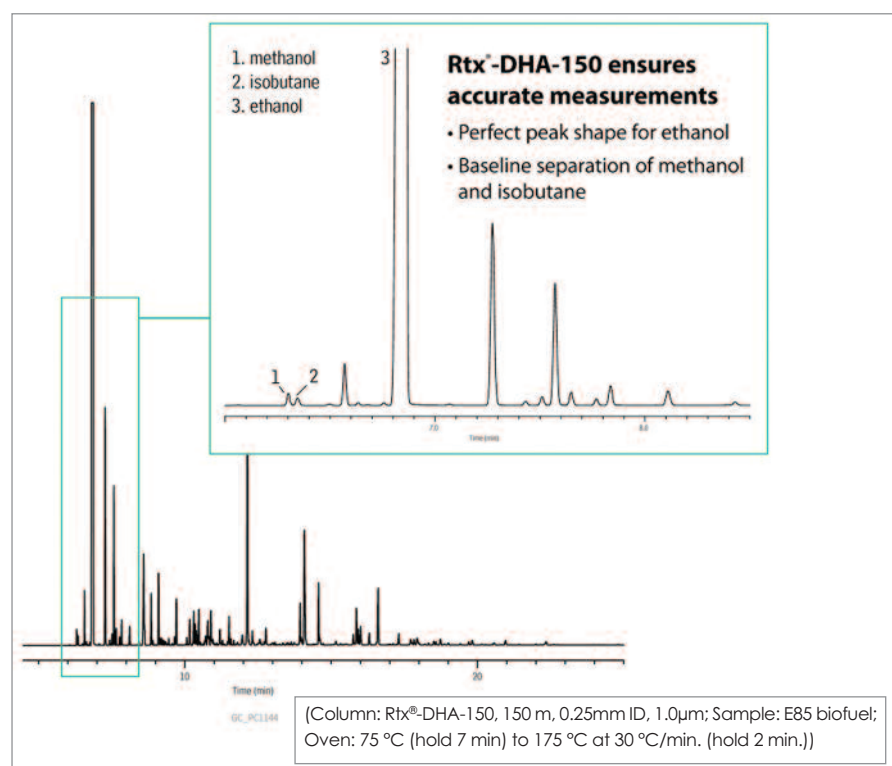


Figure 1: Sharp, symmetric alcohol peaks and complete separation of methanol and isobutane (i-C<sub>4</sub>) on the Rtx<sup>®</sup>-DHA-150 column ensure accurate quantification for E85 biofuel.

To demonstrate the performance of the Rtx<sup>®</sup>-DHA-150 column and test the assertion that a 30 meter column could provide adequate separation, denatured ethanol fuel (E85) was analyzed on both columns. As shown in Figure 1, sharp, symmetric peaks were observed for both methanol and ethanol on the Rtx<sup>®</sup>-DHA-150 column, allowing accurate quantification and elution at predictable retention times. Peak symmetry is extremely important in that state and federal laws specify the concentration of ethanol in gasoline blends, making accurate quantitation essential. In addition to excellent peak shape, complete resolution of methanol and isobutane was reliably obtained without time-consuming cryogenic conditions. Also noteworthy is that the ethanol peak exhibited virtually no tailing, an issue that has been problematic on other 150 meter columns. The limits of this column were further tested by expanding the concentration range of ethanol to 20-99%. As shown in Figure 2, excellent linearity within this expanded range was obtained ( $r^2 = 0.9993$ ). Overall, the chromatographic performance of the Rtx<sup>®</sup>-DHA-150 column was excellent and allowed accurate and uncomplicated quantitation in just 20 minutes.

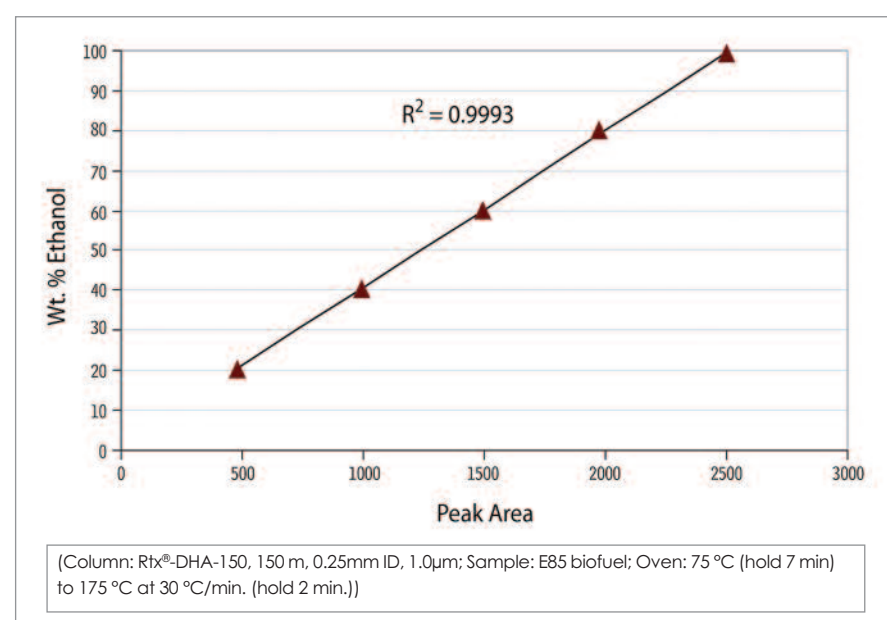


Figure 2: Rtx<sup>®</sup>-DHA-150 column for fuel ethanol analysis produces excellent linearity over a broad range (20-99%).

In contrast, results on the 30 meter column were disappointing as isobutane from the gasoline denaturant coeluted with methanol. In Figure 3, separate standards containing the alcohols and light hydrocarbons were run on a 30 meter column and compared to a denatured E85 biofuel sample under the same conditions. As is demonstrated by retention time comparison, methanol and isobutane clearly coelute in the E85 sample, meaning accurate quantification is not possible. Although fast run times could be obtained, this was of little value as the coelution of methanol and isobutane causes an overestimate of the methanol content, misrepresenting the fuel composition and affecting both sales price and fuel performance. If measuring only ethanol is desired, a shorter 100% polydimethylsiloxane column (e.g. Rtx<sup>®</sup>-1) can be used, but it will not perform according to D5501.

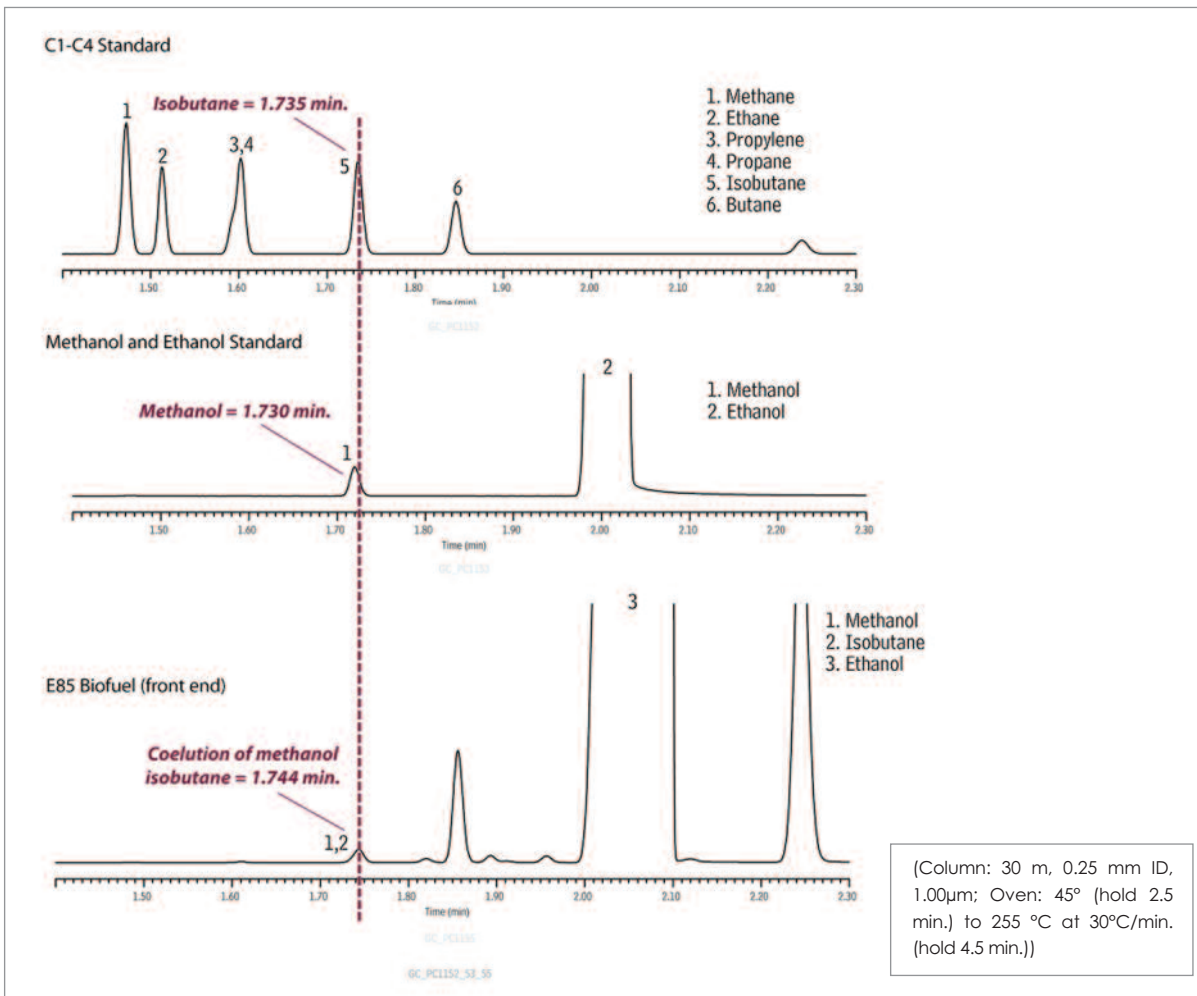


Figure 3: Isobutane coelutes with methanol on 30m bioethanol columns, preventing accurate quantification.

In conclusion, the Rtx®-DHA-150 column is the best choice for analyzing ethanol and methanol according to ASTM D5501. Excellent peak symmetry was obtained for both target alcohols and complete separation of methanol and isobutane was reliably achieved in just 20 minutes. Based on this superior performance, the Rtx®-DHA-150 column is recommended for fuel ethanol testing according to ASTM D5501.



Rtx®-DHA-150 Column: 11 pin cage fused silica