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DETERMINATION OF THE ETHANOL LEVEL IN COMMERCIAL GASOLINES BY GAS CHROMATOGRAPHY

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Abstract

The ethanol that is blended into gasolines to reduce pollution and boost octane ratings can reduce a car's performance and lead to corrosion of engine parts if the ethanol levels exceed the nominal 10% level and approach 15% (1, 2). This research describes the development of a method, using an academic grade gas chromatograph, which accurately quantifies the ethanol level in gasoline in 5 minutes. Samples of three commercial 87 octane regular gasolines and a sample of premium 93 octane gasoline were analyzed. Results indicate that all gasolines tested contained between 9% and 10% ethanol by volume.

Keywords:Gasoline, ethanol, chromatography, octane, fuel, pollution

Introduction

The Clean Air Act of 1990 mandated the use of oxygenated gasolines in areas of high air pollution (1). At the time methyl tert-butyl ether (MTBE) was the additive of choice because it had been proven to be an effective octane booster replacement for the tetraethyl lead of the leaded gasolines of the 1970's (1,2).

Both MTBE and ethanol will raise the octane rating of gasoline and in theory reduce exhaust pollution (1,2). Concerns about MTBE polluting groundwater, and the Energy Policy Act of 2005, which required that renewable fuels be blended with gasoline, led to the use of ethanol in place of some or all of MTBE in gasoline formulations (3).

Presently, a blend of 90% gasoline and 10% ethanol by volume is commonly used. The concentration of ethanol is significant because it can result in a lower engine performance.

A literature search provides several methods for analyzing gasoline composition (4). Typical analyses can run as long as 140 minutes and require multiple columns. There is an ASTM method D5599-95 for the determination of oxygenates in gasoline (5). While providing efficient separation of the oxygenates, this method requires an oxygen selective flame ionization detector. Similarly, the United States Environmental Protection Agency (EPA) has an established method that requires a selective detector and multiple columns connected in series (6).

Experimental

The gas chromatograph used in this research was an academic grade instrument. The model is Varian 3900 with Galaxie™ Data System version 1.9.3.2. The detector was a thermal conductivity detector (TCD). The column used was CP Wax 57 CB 25 mm. x .53 mm. For the development and validation of the method, a National Institute of Standards (NIST) Certified Oxygenated Gasoline Standard was obtained. (Spectrum Quality Standards http://spectrum standards.com/)

The standard contained a certified level of ethanol in a matrix comparable to commercial gasolines. The ethanol level is certified to 5.77% by weight (5.26% by volume, calculated). The techniques used in the analysis of the chromatography data that follow were adapted from Day (7) and Skoog (8).

Safety Considerations

Gasoline is highly flammable and some of the components are toxic. Proper precautions and personal protective equipment should be used.

Initial efforts to develop a method to analyze the gasolines were unsuccessful when the GC oven/column was kept at constant temperature. The varying volatilities of the gasoline components required increasing the temperature of the GC oven during the analysis. The final method (Gasoline 5 Minute Method) used to achieve resolution of the ethanol from other components is shown in Table 1. The Gasoline 5 Minute Method does not completely resolve all components of the gasoline, but does allow accurate

Table 1. Gasoline 5 Minute Method

Injector Temperature	**200 °C**
Detector Temperature	**200 °C**
Oven	**30 °C for 1 minute,**
ramp 100 °C/minute to 180 °C, hold to 5 minutes.	
Carrier Gas	**Helium 6 mL per minute**
Sample Volume	**1.0 micro liter**

determination of the ethanol in an analysis time of 5 minutes.

The chromatogram for the 5.26% volume ethanol gasoline standard, obtained using this method, is shown in Figure 1. The ethanol peak at an elution time of 1.77 minutes had a non-calibrated detector integration of 7.25% of total area.

An aliquot of the 5.26% Standard was taken and, accounting for the dilution factor, ethanol was added to bring the level up to 9.33% by volume. A second aliquot of the 5.26% Standard was taken and the ethanol level was raised to 13.40% by volume. Chromatography on these solutions was similar to Figure 1 with an increase in area of the ethanol peaks and concomitant decrease in detector response for all other components.

The chromatography on the three ethanol standards was repeated and the data are shown in Table 2. The peak areas reported were integrated by the Galaxie ™ software. The instrument used in this research does not include an auto sampler, thus the precision is directly affected by the technique of the analyst to reproducibly inject 1.0 micro liter via a syringe.

The method outlined by Day (7) was followed for relating the area of an elution band to the actual quantity of the compound. The data from Table 2 are used in the calibration curve in Figure 2, which calibrates actual percent ethanol by volume to the detector response in Percent Area.

Equation 1 derived from the line from Figure 2 can now be used in conjunction with our developed method

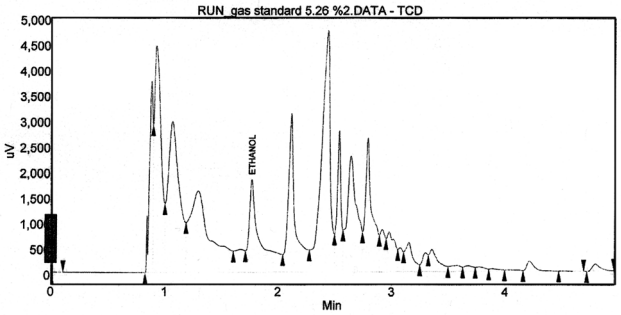

Figure 1. Gas Chromatogram of Gasoline Standard 5.26% Ethanol Volume. This is a representative chromatogram of the NIST Standard using the Gasoline 5 Minute Method.

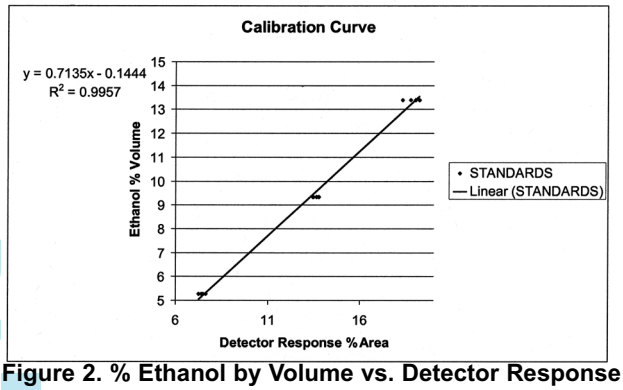

Figure 2. % Ethanol by Volume vs. Detector Response % Area. This figure illustrates the calibration of the actual volume percent of ethanol to the detector response.

to quantify % ethanol levels (y) in gasolines by inputting the detector response % area (x).

Equation 1 $Y = 0.7135 X - 0.144$

Results and Discussion

Gasoline samples were purchased from Shell, Exxon, and Speed Gas service stations in Burlington County, New Jersey, during May and June of 2009. The sampling methodology was to purchase a liter or more of gasoline in a clean dry container. About 50 milliliters of each gasoline sample were transferred to a smaller container that was kept tightly closed and at or about 25 °C. All gasolines purchased were Regular 87 Octane. In addition, a sample of Premium 93 Octane was purchased from Exxon. Figures 3 through 6 are

Table 2. Data Used to Construct Calibration Curve in Figure 2.

Gas Standard	% Area Run 1	% Area Run 2	% Area Run 3	% Area Run 4
5.26% Ethanol	**7.63**	**7.49**	**7.41**	**7.27**
9.33% Ethanol	**13.75**	**13.65**	**13.45**	**13.46**
13.40% Ethanol	**19.00**	**18.73**	**19.20**	**18.31**

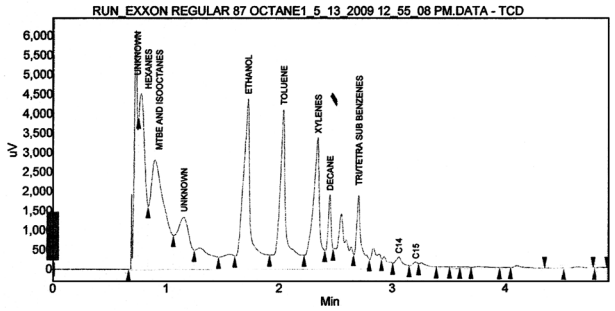

Figure 3. Gas Chromatogram of Exxon Regular 87 Octane Gasoline.

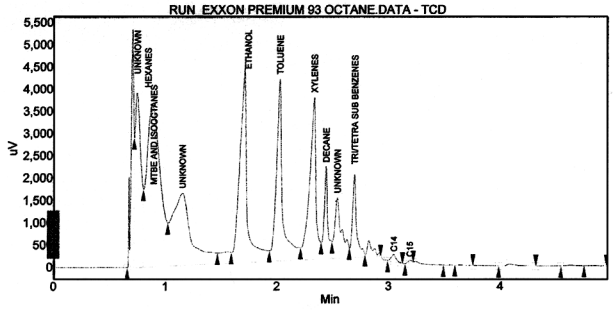

Figure 4. Gas Chromatogram of Exxon Premium 93 Octane Gasoline.

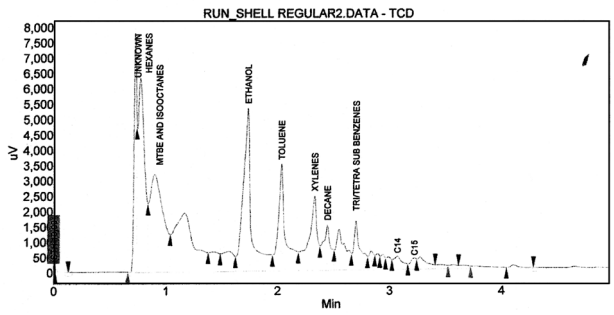

Figure 5. Gas Chromatogram of Shell Regular 87 Octane Gasoline.

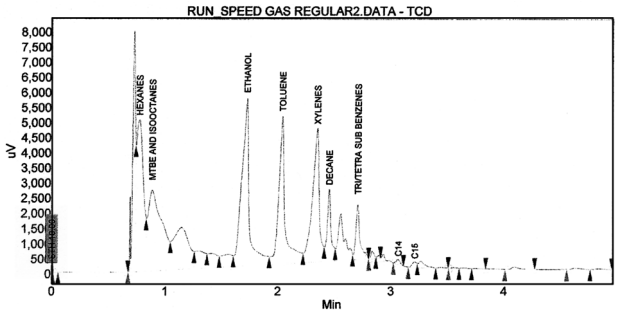

Figure 6. Gas Chromatogram of Speed Regular 87 Octane Gasoline.

representative chromatograms of the gasolines analyzed using the Gasoline 5 Minute Method. Other components of the gasolines were identified by standard addition of toluene, hexanes, xylenes, etc., and by comparison to other gasoline standards in our database.

Discussion of Ethanol Concentrations.

Table 3 details the gasolines in this study and the amount of ethanol calculated by inputting average % areas into Equation 1. The values input into the equations represent an average of 3 injections of each sample. The ethanol concentration, in all gasolines tested in this research, was close to the nominal value of 10%.

Discussion of Other Components

This research also indicated that the gasolines tested were essentially comprised of the same components. A notable observation can be seen in a comparison of Exxon Regular (Figure 3) and Exxon Premium (Figure 4). Inspection of the chromatograms at an elution time of approximately 0.8 minutes indicates the premium gasoline has a higher ratio (2.15:1) of isooctane/MTBE to hexane than the regular gasoline (1.46:1). This is consistent with the difference in the octane ratings.

Research Limitations and Other Areas of Experimentation.

1. This Gasoline 5 Minute Method developed has been optimized using the equipment at hand. It can not resolve and identify all of the gasoline components that the aforementioned ASTM and EPA methods can. The method developed in this research compliments existing methods but does not replace them. For example, the peaks identified as MTBE/isooctanes in Figures 3 through 6 are so labeled because the 2 components co-elute under the conditions of our method. It is probable that there is no MTBE in any of these samples. If additional oxygenates were added to

Table 3. Ethanol Levels in Commercial Gasolines Measured in this Research.

Gasoline	Figure	Ethanol% area	% Ethanol Calculated Using Equation 1
Exxon Regular	**3**	**13.46**	**9.46 %**
Exxon Premium	**4**	**12.80**	**9.00 %**
Shell Regular	**5**	**13.69**	**9.62 %**
Speed Regular	**6**	**13.47**	**9.47 %**

gasoline formulations, the oxygenates could possibly be erroneously identified and quantified as ethanol if the oxygenate co-elutes with ethanol using this method.

2. In addition to the incomplete chromatography, some of the peaks are not perfectly symmetrical. Experimentation with other columns, temperatures, and sample loading might result in an improved method.

3. Measurements, while reproducible from run to run, were on single point-in-time samples of each gasoline from their respective service stations. Sampling occurred during May and June. Gasoline formulations may change during different seasons of the year.

Conclusion

This research led to the development of a method that quantifies the ethanol level in gasolines accurately and efficiently. The method requires a standard gas chromatograph with programmed control of the oven temperature, but did not require multiple columns or a specific detector. Research results indicate that all regular gasolines tested are essentially comprised of the same volatile components including similar levels of ethanol. Another general outcome of the research, from a student perspective, was experience in the reverse engineering and analysis of a commercial product. This can serve as the first step in the applied research and development of an improved competitive product.

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