

Analysis of E-85 Fuel for Formic, Acetic, Propionic, Butyric, Glycolic and Citric Acids using Reversed Phase High Performance Liquid Chromatography

J. Galante-Fox
Delphi Corporation

Copyright © 2008 SAE International

ABSTRACT

An HPLC (High Performance Liquid Chromatography) method to measure the concentration of six organic acids in E-85 fuel has been developed. A three point calibration curve is established using standard solutions of the following organic acids: formic acid, acetic acid, propionic acid, butyric acid, glycolic acid and citric acid. An internal standard (maleic acid) is used to monitor HPLC system suitability and peak retention time stability. The method utilizes UV detection at 210 nm to detect and quantify the levels of each acid in E-85 fuel. Test results from nine commercially available E-85 fuel samples are reported.

Analytical method validation was achieved by performing and confirming system suitability or injection repeatability (percent relative standard deviation $\leq 3\%$), calibration curve linearity ($R^2 \geq 0.999$), analysis repeatability (standard deviation < 1 mg/L) and recovery (percent recovery 91 – 102%). The minimum detectable level was determined to be less than 1.5 mg/L for each acid.

INTRODUCTION

E-85 fuel corrosivity can have a negative impact on fuel system component durability performance. Contamination of the fuel with chloride and water from the ethanol and E-85 distribution systems can have a significant impact on fuel injector performance. In addition, organic acids from the ethanol fermentation process can contribute to the overall corrosivity of the fuel [1].

The ethanol fermentation process converts sugars to ethanol and carbon dioxide. As a result of the many chemical reactions that take place during the process, organic acid byproducts can form. The most common organic acid found in E-85 is acetic acid; however formic acid, glycolic acid and propionic acid have also been

detected in commercial E-85 samples. An analytical method was needed to quantify organic acid levels in commercial E-85 fuels to support investigations of fuel system component durability.

A reversed phase HPLC method was developed for the analysis of E-85 fuel based on a published method used to analyze dairy products for 11 different organic acids [2]. This method used an external standard method to determine the concentration of organic acids. For analysis of E-85 fuel, modifications were made to the sample preparation procedure and the mobile phase gradient program resulting in a test procedure that can be used for the analysis of formic, acetic, propionic, butyric, glycolic and citric acids.

Validation of the analytical procedure was accomplished by following the guidelines in references [3] and [4].

This analytical method was not designed to be used for quality control and high throughput of samples. The method is more appropriate for use in E-85 fuel quality investigations.

EXPERIMENTAL

SAFETY

The MSDS (Material Safety Data Sheet) for each chemical used in the test method was reviewed carefully before use. The organic acids are corrosive and can cause burns. Preparation of all solutions was performed in a ventilation hood to avoid breathing vapors.

EQUIPMENT AND OPERATING CONDITIONS

The analysis was performed using a Waters Alliance 2695 Separations Module equipped with a 2487 Dual Wavelength Absorbance detector set at 210 nm (Waters Corporation, Milford MA, USA). Instrument parameters are shown in Table 1.

TABLE 1: HPLC SYSTEM SET-UP

Column	Atlantis dC ₁₈ , 250 mm x 4.6mm, 5 µm (Waters)
Guard column	Atlantis dC ₁₈ , 5 µm (Waters)
Flow rate	1.5 ml/min
Temperature	30 °C (column heater); 27 °C (sample)
Injection volume	30 microliters (µl)
UV Detector	210 nanometers
Mobile Phase	1% acetonitrile in 20 milli-Molar phosphate buffer at pH 2.2
Run time	30 minutes

CHEMICALS

All standards and chemicals were purchased at the highest available purity from Sigma-Aldrich Company, with the exception of HPLC grade water, HPLC grade acetonitrile and HPLC grade methanol purchased from Fisher Scientific.

Secondary standards prepared using the high purity chemicals from Sigma-Aldrich Company were considered acceptable for this analysis. Calculations using the lowest and highest possible purity values gave a maximum difference of 0.3 milligrams / Liter (mg/L) organic acid in E-85 fuel. This difference was considered acceptable for the purposes of typical E-85 fuel quality investigations.

MOBILE PHASE AND DILUENT PREPARATION

Mobile Phase: Twenty (20) millimoles of sodium phosphate monobasic (NaH₂PO₄) in HPLC grade water was adjusted to pH 2.2 with phosphoric acid. This phosphate buffer solution was prepared fresh daily. One (1) volume percent HPLC grade acetonitrile was diluted in this phosphate buffer to prepare the mobile phase.

Sample and standard diluent: Approximately 1 mg/L of maleic acid in mobile phase was prepared as the sample and standard diluent solution.

STANDARD PREPARATION

Standard solutions containing formic acid, acetic acid, propionic acid, butyric acid, glycolic acid and citric acid were prepared fresh for each analysis by diluting in standard diluent containing internal standard (maleic acid). Three working standards at nominal concentrations of 8, 32 and 80 mg/L of each organic acid were prepared. Stock standard organic acid concentrations were calculated taking into account the purity of the secondary standard.

SAMPLE PREPARATION

Each E-85 fuel sample was prepared using the procedure in steps 1 - 4 below. A blank sample (no fuel) was also prepared and injected at least every 4 sample injections to demonstrate absence of contamination and organic acid carryover.

Step 1: Using a volumetric pipette, transfer 50 milliliters (ml) of E-85 fuel into a glass container and add 2 ml of 0.5 Molar sodium hydroxide. Cover and stir for 15 minutes.

Step 2: Evaporate the solution to dryness using mild heat (< 50 °C). Cool to room temperature.

Step 3: Add 10 ml of sample diluent solution and 250 microliters (µl) of concentrated phosphoric acid. Cover and stir for 15 minutes.

Step 4: Sample dilution may be necessary if the concentration(s) of acid(s) is(are) outside the calibration curve range. If dilution is necessary, accurately and volumetrically dilute the solution prepared in step 3 with sample diluent. The dilution factor is then used to calculate the final organic acid concentration in the E-85 fuel sample.

RECOVERY SAMPLE PREPARATION

Five separate solutions containing the six organic acids at a nominal concentration of 8 mg/L (each) were prepared by diluting the organic acids in a blend of 85 volume percent fuel grade ethanol and 15 volume percent U.S. EPA Emission Certification Test Fuel [5]. Each solution was then analyzed for organic acid concentration following the procedures detailed in this manuscript. Percent recovery was calculated based on the theoretical amount of organic acid in the solution and the analytical method results.

RESULTS AND DISCUSSION

As with all analytical procedures, unusual or unexpected results should be confirmed using a separate analytical method or analysis technique. Peak interferences from E-85 fuel degradation products, additives and contaminants are possible.

CHROMATOGRAPHY

Figure 1 shows a chromatogram of a typical standard injection. Figure 2 expands the chromatogram from 0 to 6 minutes. Although baseline resolution is not achieved for glycolic and formic acids, and maleic and citric acids, peak height can be used successfully for calibration and quantification of organic acid concentrations.

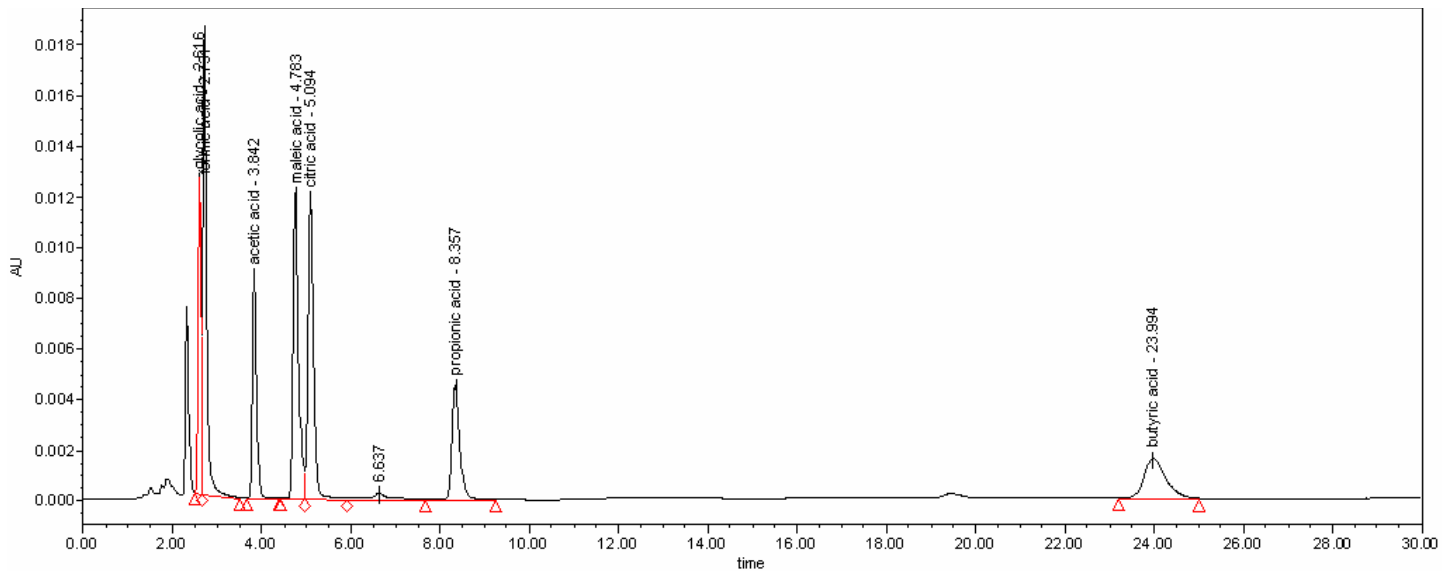


FIGURE 1: Typical standard chromatogram

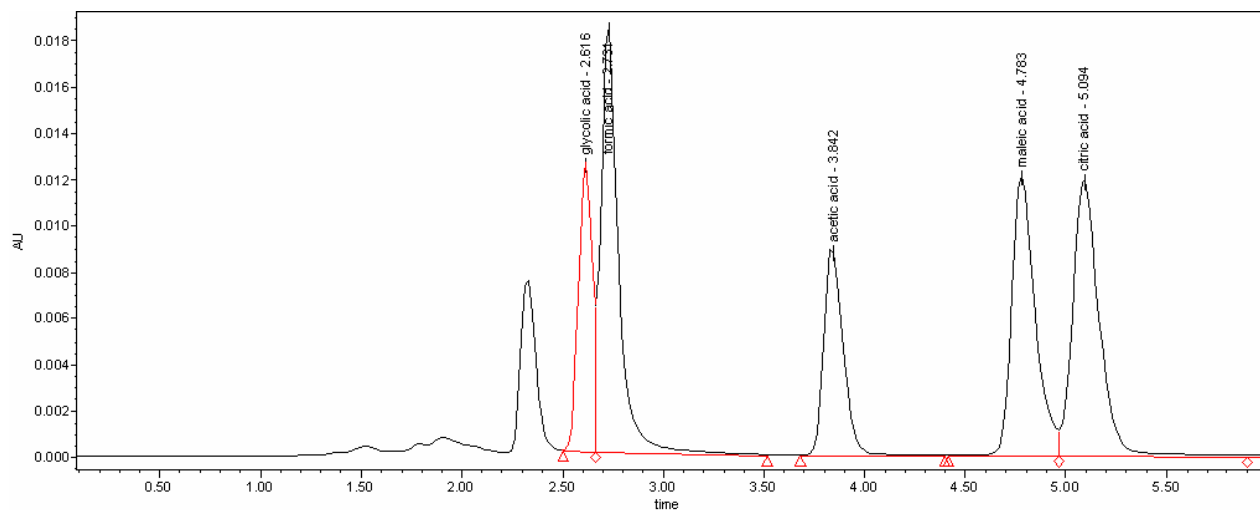


FIGURE 2: Typical standard chromatogram, 0 – 6 minutes

RETENTION TIME STABILITY

Table 2 summarizes the organic acid peak retention times for multiple injections in 1 day. Very little variation in peak retention time was observed. The highest percent relative standard deviation (%RSD) was for butyric acid (0.5 %RSD).

Run-to-run (day-to-day) retention time variation can be significant due to variations in preparation and pH adjustment of the mobile phase. An internal standard (maleic acid) is used to monitor peak retention times to account for this variation.