



Guidelines for Establishing Ethanol Plant Quality Assurance and Quality Control Programs

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Introduction

The Renewable Fuels Association (RFA) is the national trade association for the U.S. fuel ethanol industry. Membership is comprised of numerous ethanol producers, both large and small, as well as suppliers to the industry and other interested parties. Founded in 1981, the RFA's primary objective is to promote public policy initiatives that increase the market for fuel grade ethanol produced from a variety of feed stocks including grains, agricultural wastes, and various biomass feedstock sources.

As the ethanol industry has grown, so has the Renewable Fuels Association's areas of responsibility to its membership. Today the RFA not only focuses on legislative/regulatory and public policy type issues but also maintains several committees and task groups to address industry needs. These committees include a technical committee to address various technical issues and to assist with technical industry publications (such as this one); an education and promotion committee that seeks to educate consumers and organizations as well as to identify, assess, and pursue opportunities for market growth; and a membership committee. In addition, there is a fuel cell task force working to pursue opportunities to use ethanol in fuel cell applications. These committees and task forces are comprised of representatives of our member companies, staff, and when necessary technical consultants and other interested stakeholders. The RFA, through its research and education arm, the "Renewable Fuels Foundation" provides the support structure for the E diesel Consortium. The E diesel Consortium is a standing committee of the Renewable Fuels Foundation and is comprised of various stakeholder companies and organizations. The E diesel Consortium is exploring the potential commercialization pathways for diesel ethanol blends.

The RFA promotes the use of fuel grade ethanol in all its various applications. This includes not only E-10 (90% gasoline/10% ethanol), reformulated gasoline (RFG), and oxygenated fuels, but developing markets such as E-85 (15% gasoline/85% ethanol). The RFA is also working on various developing applications such as fuel cell applications and E diesel, a cleaner burning diesel fuel containing up to 15% ethanol.

This document focuses on the product quality and integrity "Fuel Ethanol" (E-95), which is of the utmost importance to the Renewable Fuels Association and its members. To achieve quality laboratory data for fuel ethanol products, the Renewable Fuels Association has put together this information, which includes a discussion of methods for analyses, sampling, general laboratory equipment and techniques and instruction on quality assurance and quality control practices. The purpose of this document is to serve as a condensed technical reference for ethanol producers, ethanol blenders, and other interested parties who need such information.

For an expanded discussion of the importance of specifications and properties of fuel grade ethanol, technical/laboratory personnel may wish to review RFA Publication # 960501 "Fuel Ethanol-Industry Guidelines, Specifications and Procedures." This document and other RFA publications are available on the RFA website at www.ethanolrfa.org. If you have any questions about the contents of this document, feel free to contact us. Our contact information is as follows:

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Fuel Ethanol (E-95) product quality and integrity is important to the Renewable Fuels Association. To achieve quality laboratory data for fuel ethanol products, the Renewable Fuels Association has put together this information, which includes a discussion of methods for analyses, sampling, general laboratory equipment and techniques and instruction on quality assurance and quality control practices.

Quality Assurance (QA) is a set of operating principles that, when strictly followed during sample collection and analysis, will produce data of known and legally defensible quality. Quality Control (QC) is a measure within a sample analysis methodology to assure that the process is in control. Although all analysts practice quality control somewhat instinctively, under actual working conditions, sufficiently detailed QC may be neglected. An established routine Quality Assurance program applied to each analytical test can relieve analysts of the necessity of originating individual QC efforts.

Quality Assurance programs have two primary functions in the laboratory. First the program should continually monitor the reliability (accuracy and precision) of the results being reported. They should answer the question “How good (accurate and precise) are the results obtained?” This function is the *determination* of quality. The second function is the *control* of quality to meet the program requirements for reliability. Each analytical method has a rigid protocol. Similarly, QC associated with a test must include definite required steps for monitoring the test and insuring results are correct. The steps in QC vary with the type of analysis. For example, in titration, standardization of the titrant on a frequent basis is an element of QC. In any instrumental method, calibrating and checking out of instrument response are also QC functions. All of the testing variables that affect the final results should be considered, evaluated and controlled.

Company Quality Assurance Programs ensure that the sampling methods produce representative samples, confirm that laboratory analyses are reliable, and verify that the reported results are suitable to support decisions, and measure and document any uncertainty in analytical data. Each laboratory should have a written Quality Assurance Plan. This plan should include details of program management, standard operating procedures and process assessment. The plan should describe sampling and analytical procedures and frequencies. The methods used should be described in detail, such that an experienced analyst unfamiliar with the method can obtain acceptable results. The lab should also have reference materials on hand, such as the Annual Book of ASTM Standards. Other plan elements included in the QA Plan are documentation and record keeping requirements, instrument calibration method and frequency, quality control requirements, lab safety, and training.

This document is not intended to be a company QA plan but is included as a suggested minimum requirement for producing valid lab results and assuring fuel ethanol (E-95) product quality meets customer requirements.

The ASTM International (ASTM) maintains the approved written analytical procedures for assuring denatured fuel ethanol quality. The ASTM D 4806; *Standard Specification for Denatured Fuel Ethanol for Blending with Gasoline's for use as an Automotive Spark-Ignition Engine Fuel* is the industry standard. The following table describes the testing parameters with limits as well as suggested testing frequencies.

<u>Quality Parameter</u>	<u>Limits</u>	<u>ASTM Test Procedure</u>	<u>Testing Frequency/Location</u>
Ethanol volume %, min	92.1	D5501-94 (1998) e1	Each batch / in house
Methanol, volume %, max	0.5	D5501-94 (1998) e1	Each batch / in house
Water content, vol %, max	1.0	E1064-04, E203-01	Each batch / in house
Acidity (as acetic acid) weight %, max (mg/L)	0.0070 (56)	D1613-02	Each batch / in house
pHe	6.5 –9.0	D6423-99	Each batch / in house
Copper content, mg/kg, max	0.1	D1688-02	Quarterly / Third Party Laboratory
Inorganic Chloride Content, ppm (mg/L)	40 (32)	D512-81 (1985), Procedure C, modified	Quarterly / Third Party Laboratory
Solvent washed gum, mg/100mL, max	5	D381-03	Quarterly / Third Party Laboratory
Appearance	Clear and Bright, Free from suspended or settle particulate matter	Visual Examination at room temperature	Each batch / in house
Sulfur ppm max	30	ASTM D4806	Quarterly / Third Party Laboratory

In addition to the industry standard, the State of California Air Resources Board (CARB) has passed legislation governing the specifications of denatured fuel ethanol to be blended into California Reformulated Gasoline. Please note that the test procedures versions for acidity, copper content and solvent washed gum are earlier versions of ASTM methods than noted in the above table. This is governed by CARB, not ASTM.

<u>Quality Parameter</u>	<u>Limits</u>	<u>ASTM Test Procedure</u>	<u>Testing Frequency/Location</u>
Sulfur ppm, max	10	ASTM D5453-93	Quarterly / Third Party Laboratory
Benzene, vol %, max	0.06	ASTM D5580-00	Each batch / based on denaturant concentration
Aromatics, vol %, max	1.7	ASTM D5580-00	Each batch / based on denaturant concentration
Olefins, vol %, max	0.5	ASTM D6550-00	Each batch / based on denaturant concentration
Acidity (as acetic acid) weight %, max (mg/L)	0.0070 (56)	<i>D1613-96</i>	Each batch / in house
Copper content, mg/kg, max	0.1	<i>D1688-95, Test Method A</i>	Quarterly / Third Party Laboratory
Solvent washed gum, mg/100mL, max	5	<i>D381-00</i>	Quarterly / Third Party Laboratory

Further, CARB has passed regulations governing the specifications for denaturant to be blended into denatured fuel ethanol. The specifications, limits and test procedures are outlined in the table below.

<u>Quality Parameter</u>	<u>Limits</u>	<u>ASTM Test Procedure</u>	<u>Testing Frequency/Location</u>
Benzene, vol %, max	1.1	ASTM D5580-00	Each batch / denaturant C of A
Aromatics, vol %, max	35	ASTM D5580-00	Each batch / denaturant C of A
Olefins, vol %, max	10	ASTM D6550-00	Each batch / denaturant C of A

Note that there are exceptions to the above California limits based on the properties of the gasoline to which the ethanol is added. Those producers who distribute ethanol for use in California must meet the above specifications unless otherwise agreed to by a refiner who indicates it can accept non-conforming ethanol for use in its gasoline and still meet the exception rules. If a producer intends to market under such an exception, they should conduct a detailed review of the applicable California regulations.

The technical procedure for sampling products can be an in-house procedure or an ASTM approved procedure. ASTM D4057 Practice for Manual Sampling of Petroleum and Petroleum Products can be used and adapted for sampling denatured fuel ethanol.

Each producer should establish and maintain a batch /lot or similar system of production. Each “batch” should be sampled and tested with the analytical procedures outlined above. The results of the approved lot should be documented in a Certificate of Analysis (C of A). The C of A must contain the following information: producer name and location, date of manufacture, lot number and quality parameter results. This certificate provides for the traceability of product in a commingled system and should accompany each load of fuel ethanol transported from the facility.

Each laboratory should have a written program for instrument calibration. Calibration checks and samples should be documented. Each laboratory should provide for data verification and validation also. This can be accomplished by running known samples or participation in inter-laboratory cross check programs.

All lab employees should be properly trained in all aspects of the QA Plan from proper sampling to lab QA to individual QC including safety and hazardous materials training.

Sample management procedures should identify collection, frequency and documentation procedures. The plan should also provide for retaining individual samples. Each sample should be labeled and stored properly for future identification if necessary.

Shipment vessels should be sealed and labeled according to the Department of Transportation Hazardous Materials Shipping Requirements. *If you ship fuel ethanol products, truck or rail, you are required to be registered with the DOT.* The appropriate wording for the Bill of Lading is the following:

UN 1987, Alcohols, n.o.s. (ethanol, gasoline), Hazard Class 3, Packing Group II.

Furthermore, a Material Safety Data Sheet should accompany the Bill of Lading and C of A.

To assure quality product at delivery it may be necessary to maintain a dedicated rail fleet. If your rail fleet is not dedicated, third party contract carriers should be apprised of appropriate prior backhauls. The approved prior backhauls for denatured fuel ethanol are the following: denatured fuel ethanol, natural gasoline, unleaded gasoline or gasoline components. Each shipment of denatured fuel ethanol is recommended to contain an approved corrosion inhibitor at the vendor recommended treat rate.

Additional information on transportation recommendations and shipment vessel labeling requirements are contained within RFA Publication #960501 “Fuel Ethanol-Industry Guidelines, Specifications and Procedures.”

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