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California Energy Commission
Clean Transportation Program

FINAL PROJECT REPORT

Measurement and Standards Requirements for Hydrogen and Biodiesel Used as a Transportation Fuel

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Prepared by: California Department of Food and Agriculture,
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Gavin Newsom, Governor

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Chapter 1:
John Mough
Kevin Schnepp
Pamela Fitch
Chapter 2:
R. Norman Ingram
Pamela Fitch
Chapter 3:
Samuel Ferris
Pamela Fitch
Primary Authors

California Department of Food and Agriculture,
Division of Measurement Standards
6790 Florin-Perkins Road, Suite 100
Sacramento, CA 95828-1812
(916) 229-3000
CDFA Website: www.cdfa.ca.gov

Contract Number: 600-09-015

Tobias Muench
Sarah K. Williams
Contract Managers

Mark Wenzel
Office Manager
ADVANCED VEHICLE INFRASTRUCTURE OFFICE

John P. Butler II
Acting Deputy Director
FUELS AND TRANSPORTATION

Drew Bohan
Executive Director

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Chapter 1 Hydrogen Fuel Quality:

California Department of Food and Agriculture
Kristin Macey
R. Allan Morrison, Jr.
Kevin Batchelor
Steven Cook
Ron Nies
Roger Macey
Karen Green
Rebecca Bland
Amber Schaffner
Tammy Sulli
Ramsey Airada

California Fuel Cell Partnership
Jennifer Hamilton
Catherine Dunwoody

California State University, Los Angeles
David Blekhman

California Air Resources Board
Michael Kashuba
Gerhard Achtelik

Lotus Consulting
Randy Cook
Edward Cook

Bruker Daltonics, Inc.
Ed Nygren

Toyota Motor Corporation
Jackie Birdsall

iCONNECT
Chris Petty
Robert Miller

California Energy Commission
Jean Baronas
Jim McKinney
Pat Perez
Randy Roesser
John Butler

ASTM D03 Committee

Chapter 2 Hydrogen Metrology Standards:

California Department of Food and Agriculture

Kristin Macey
Steven Cook
R. Allan Morrison, Jr.
Ron Nies
Kevin Batchelor
David Hawkins
Roger Macey
Greg Boers
Dan Reiswig
John Roach
Van Thompson
Janice Price
Jennifer Crow
Karen Green
Rebecca Bland
Amber Schaffner
Tammy Sulli

California Energy Commission

Jean Baronas
Jim McKinney
Pat Perez
Randy Roesser
John Butler

National Renewable Energy Laboratory

Chad Blake
Robert Burgess
Marc Butler
William Buttner
Kevin Harrison
Michael Peters
Matthew Post
Carl Rivkin
Carrieann McDonough
Joanne Greeley

National Institute of Standards and Technology Office of Weights and Measures

Members of U.S. National Work Group for the Development of Hydrogen Measurement Technology

Chapter 3 Physical and Chemical Analysis of Biodiesel Fuel:

California Department of Food and Agriculture
Kristin Macey
R. Allan Morrison, Jr.
Kevin Batchelor
Steven Cook
Ron Nies
Richard Uyehara
David Hawkins
Karen Green
Rebecca Bland
Amber Schaffner
Tammy Sulli
Roger Macey

California Energy Commission
Jean Baronas
Akasha Kaur Khalsa
Jim McKinney
Pat Perez
Randy Roesser
John Butler

PREFACE

Assembly Bill 118 (Núñez, Chapter 750, Statutes of 2007) created the Clean Transportation Program, formerly known as the Alternative and Renewable Fuel and Vehicle Technology Program. The statute authorizes the California Energy Commission (CEC) to develop and deploy alternative and renewable fuels and advanced transportation technologies to help attain the state's climate change policies. Assembly Bill 8 (Perea, Chapter 401, Statutes of 2013) reauthorizes the Clean Transportation Program through January 1, 2024, and specifies that the CEC allocate up to $20 million per year (or up to 20 percent of each fiscal year's funds) in funding for hydrogen station development until at least 100 stations are operational.

The Clean Transportation Program has an annual budget of about $100 million and provides financial support for projects that:

- Reduce California's use and dependence on petroleum transportation fuels and increase the use of alternative and renewable fuels and advanced vehicle technologies.
- Produce sustainable alternative and renewable low-carbon fuels in California.
- Expand alternative fueling infrastructure and fueling stations.
- Improve the efficiency, performance and market viability of alternative light-, medium-, and heavy-duty vehicle technologies.
- Retrofit medium- and heavy-duty on-road and nonroad vehicle fleets to alternative technologies or fuel use.
- Expand the alternative fueling infrastructure available to existing fleets, public transit, and transportation corridors.
- Establish workforce-training programs and conduct public outreach on the benefits of alternative transportation fuels and vehicle technologies.

Under California's Business and Professions Code, the Division of Measurement Standards regulates the sale of transportation fuels in California and is responsible for the enforcement of fuel quality standards. By law, the State adopts test procedures and fuel quality standards published by recognized independent consensus standards organizations. The CEC entered into Contract 600-09-015, "Measurement and Standards Requirements for Hydrogen and Biodiesel" with the Department of Food and Agriculture to address the need for new regulations and test procedures to support the expanded use of hydrogen fuel and biodiesel in California.

ABSTRACT

This project was funded by a contract of the California Energy Commission with the California Department of Food and Agriculture/Division of Measurement Standards as part of its Clean Transportation Program. This program aims to develop and deploy alternative and renewable fuels and advanced transportation technologies in California to promote the state's climate change and clean air goals and reduce petroleum dependence. This report has three chapters, which address Hydrogen Fuel Quality, Development of Measurement Standards for Gaseous Hydrogen Fuel Sold at retail in California, and the Physical and Chemical Analysis of Biodiesel.

One of the goals of this program is to promote a substantial increase in the number of fuel cell electric vehicles (FCEVs) in California. Major automobile manufacturers are introducing hydrogen-powered FCEVs. An expansion of the hydrogen refueling infrastructure will be needed to service these cars. New codes and regulations, and approved hydrogen dispensers, are required for the retail sale of hydrogen in California.

The California Department of Food and Agriculture oversees the sale of transportation fuels in California. California Business and Professions Code Division 5, Chapter 14, Sections 13446 and 13450 require the Department to establish and enforce quality specifications for hydrogen fuel and biodiesel, respectively. The sale of hydrogen fuel in California will also require the California Department of Food and to develop specifications and tolerances for commercial hydrogen fuel dispensers. Reference metrology standards are needed for field testing and type evaluation of these dispensers, as required by state law.

A second goal of the program is to increase the use of biodiesel in California to improve air quality and reduce dependence on petroleum products. Existing standards and specifications support the sale of biodiesel in blends up to 20 percent, as well as 100 percent biodiesel. This project was designed to produce data to support new specifications and test methods for quality to cover the range between 20 and 100 percent.

The CEC provided funding for the development of standards and specifications for hydrogen dispensers, hydrogen fuel, and biodiesel. The results described in this report will be shared with consensus standards development organizations and other stakeholders.

Keywords: California Department of Food and Agriculture/ Division of Measurement Standards, National Conference on Weights and Measures, National Institute of Standards and Technology, metrology, method of sale, SAE International, ASTM International, hydrogen fuel, hydrogen dispensers, type evaluation, type testing, National Renewable Energy Laboratory, hydrogen test methods, alternative fuels, biodiesel.

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EXECUTIVE SUMMARY

The California Energy Commission (CEC) and the Air Resources Board have set goals to improve air quality and reduce petroleum dependence in California. These include a reduction of petroleum fuel use to 15 percent below 2003 levels by 2020 and the reduction of greenhouse gas emissions to 80 percent below 1990 levels by 2050. To achieve these goals, alternative fuels are targeted to reach 20 percent of all fuel consumed in California by 2020.

Hydrogen used to power fuel cell vehicles and biodiesel fuel for compression ignition engines will play critical roles in meeting California’s alternative fuel use goals. However, significantly expanding the use of these fuels will require changes to the codes and regulations that govern the retail sale of transportation fuels in California. In addition, the sale of large numbers of fuel cell passenger cars will require a significant expansion of the State’s hydrogen refueling infrastructure.

This project was undertaken by the California Department of Food and Agriculture's Division of Measurement Standards (DMS) with funding from the CEC. Three separate tasks were identified: the evaluation of methods for testing hydrogen fuel quality; the development of standards and regulations required for retail hydrogen fuel dispensers in California; and the evaluation of test methods for biodiesel blends above 20 volume percent. A brief overview of each of these tasks is given below. The full reports for each task follow as separate chapters of this report.

Chapter 1: Hydrogen Fuel Quality: Methods for Analysis of Contaminants in Gaseous Hydrogen Fuel

Chapter 14, Section 13446 of the Business and Professions Code requires the DMS to establish and enforce quality specifications for transportation fuels in California. Section 13401 of the Code classifies hydrogen for vehicles as a transportation fuel, making the California Department of Food and Agriculture responsible for regulating the quality of hydrogen fuel in the state.

A very high purity grade of hydrogen is required to protect the catalysts used in fuel cell engines. A wide range of contaminants can adversely affect the fuel cell performance, even at extremely low concentrations. Existing analytical methods for hydrogen gas lack the high sensitivity and robustness required for reliable measurements at very low levels and may be subject to various interferences. Quality standards for hydrogen fuel were published in 2011 as SAE International’s *Surface Vehicle Standard J2719 - Hydrogen Fuel Quality for Fuel Cell Vehicles*. *SAE J2719* has been adopted by reference by the Department of Food and Agriculture in California Code of Regulations Title 4, Division 9, Chapter 6, Article 8, Section 4181. *SAE J2719* sets maximum contaminant levels for impurities of concern specifically for hydrogen fuel. Contaminants in hydrogen fuel not only reduce fuel cell efficiency, but also can rapidly and irreversibly degrade the catalyst, requiring an expensive replacement.

To be enforceable, the specifications of *SAE J2719* must be supported by validated test methods that can be used to demonstrate compliance. Such methods are published by consensus standards organizations such as American Society for Testing and Material (ASTM International). Existing hydrogen test methods were developed for industries such as food and metallurgy. Fuel cells have more stringent purity requirements than those applications. Current test methods generally do not have sufficient sensitivity and robustness for the analysis of hydrogen for fuel cells. Therefore, they cannot support regulatory enforcement by the California Department of Food and Agriculture. In some cases, validated consensus methods for the analysis of *SAE J2719* contaminants in hydrogen gas do not exist.

The development of hydrogen fuel quality test methods under this project had three components. First, a survey and evaluation of existing test methods for assessing hydrogen fuel purity is conducted. Second, existing methods that are adequate for the analysis of hydrogen fuel quality are validated. Finally, areas in which further work is needed to develop adequate test methods are identified. The results of this work is shared with ASTM members and other stakeholders to promote the development of a suite of consensus test methods to support regulation of quality standards for hydrogen fuel in California. In turn, this will promote the development of the hydrogen infrastructure essential for the acceptance of fuel cell vehicles by consumers.

Chapter 2: Development of Measurement Standards for Gaseous Hydrogen Fuel Sold at Retail in California

Hydrogen fuel cells power a wide range of vehicles. Growing numbers of transit systems throughout California are using fuel cell buses. Large numbers of fuel cell forklifts and similar vehicles are in use in industrial and warehouse settings. A limited number of fuel cell passenger cars are currently leased to consumers in California in demonstration programs. Several manufacturers plan to begin selling fuel cell passenger cars between 2015 and 2017.

A handful of hydrogen refueling stations have been constructed to service these vehicles. Most of these are privately owned and offer limited or no public access. The manufacturers of leased fuel cell cars provide refueling as part of their lease agreements. Public access to a greatly expanded hydrogen refueling infrastructure is essential to support the retail sale of fuel cell vehicles in California.

California BPC, Division 5, Section 12500.5 requires that commercial fuel dispensing devices be approved by the Division of Measurement Standards of the California Department of Food and Agriculture to ensure they meet all metrological requirements. BPC Section 12107 requires the Department to adopt by reference the latest specifications and tolerances for all commercial fuel dispensing devices. It also requires that device specifications and tolerances developed by the National Conference on Weights and Measures be adopted when published by the National Institute of Standards and Technology in its *Handbook 44 Specifications, Tolerances, and Other Technical Requirements for Weighing and Measuring Devices***.**

Prior to 2007, no specifications or tolerances for hydrogen fuel dispensers had been developed. For such situations, *Handbook 44* provides procedures for their approval as unclassified devices. However, without device-specific protocols, there is the possibility that different evaluators might require different performance measures. Because of this situation, and the limited market for commercial hydrogen dispensers, device manufacturers have been reluctant to invest in their development. This represents an obstacle to the sale of fuel cell vehicles in California.

To address the need for clear specifications and tolerances for hydrogen dispensers, the CEC provided funding to the California Department of Food and Agriculture for the development of testing and certification protocols for hydrogen dispensers. Chapter 2 of this report, *Development of Measurement Standards for Gaseous Hydrogen Fuel Sold at Retail in*

California, describes the specifications, tolerances, and method of sale that have been adopted by California and nationally as part of this project.

In addition, three metrological standards (gravimetric, volumetric, and master meter) for the testing and type evaluation of hydrogen fuel dispensers were developed and tested as part of this project. These standards were designed and constructed under an agreement with the National Renewable Energy Laboratory in Golden, Colorado. These standards were incorporated into one mobile device, the Hydrogen Field Standard. Test data from the Hydrogen Field Standard showed that the gravimetric standard met the required tolerances for type evaluation of hydrogen dispensers. The volumetric and master meter standards failed to meet the required tolerances. Testing of dispensers at retail stations throughout California is underway using the gravimetric standard of the Hydrogen Field Standard. Data is also being collected with the volumetric and master meter standards to better understand their performance. Results of this testing, with confidential business information removed, will be shared with stakeholders.

Chapter 3: Physical and Chemical Analysis of Biodiesel

Fuel tax figures from the Board of Equalization show that California's monthly consumption of diesel fuel averages over 200 million gallons. The combustion of petroleum-based diesel fuel is a leading source of greenhouse gas and toxic emissions in California and around the world. These emissions are major contributors to global warming and climate change and have many significant adverse public health impacts.

Biodiesel fuel is a renewable fuel that can substitute for No. 2 diesel fuel in compression ignition engines. Although these engines can run on pure biodiesel fuel, it is usually blended with petroleum diesel. Biodiesel blends significantly reduce greenhouse gas and most toxic tailpipe emissions compared to petroleum diesel. Increased use of biodiesel blends in California will reduce dependence on petroleum products. At concentrations up to 5 percent, biodiesel has no deleterious effects on the required specifications of diesel fuel. As a result, these low-level blends may be marketed with no special labeling or other requirements.

California BPC Division 5, Chapter 14, Section 13450 requires the DMS to establish and enforce quality specifications for compression ignition engine fuel in California. Section 13450 requires the Department to adopt standard specifications for diesel fuel published by ASTM International or another recognized consensus organizations. ASTM International has published standard specifications for pure (neat) biodiesel (ASTM *D6751*), and blends between 6 and 20 volume percent biodiesel with petroleum diesel fuel (ASTM *D746),* along with a suite of validated test methods for establishing compliance with these standards.

Currently, there are no standard specifications or validated test methods for biodiesel blends above 20 volume percent. Such specifications and test methods are needed to support commercialization of higher biodiesel blends in California. When such specifications do not exist, the California Department of Food and Agriculture may be required to develop interim specifications. In the absence of standard specifications, transportation fuels may be sold in California only with a developmental fuel variance from the California Department of Food and Agriculture.

Biodiesel has very different physical and chemical characteristics than conventional diesel fuel. Analytical methods developed for petroleum diesel may not be appropriate for biodiesel blends above 20 volume percent. Research is needed to identify which of the existing methods can be applied to higher biodiesel blends and which methods need modifications.

The activities conducted my DMS and reported in Chapter 3 were designed to evaluate existing diesel and biodiesel test methods for blends with concentrations above 20 volume percent. Each blend stock was mixed with petroleum diesel fuel to prepare a series of blends covering the range of 20 – 90 percent biodiesel. Each blend, along with the neat blend stocks, was tested using ten ASTM diesel and biodiesel test methods to determine the suitability of the methods over the entire concentration range of blends. Eight of the methods tested worked for all blends tested. Two distillation test methods failed for most of the blend concentrations. Possible alternative test methods are identified as replacements for these two tests.

ASTM approved the establishment of a new workgroup to develop standard specifications for biodiesel blends above B20 at its June 2013 meeting in Montreal. Allan Morrison, Senior Environmental Scientist at DMS is taking a lead role in this effort. The results of this project will be shared with this workgroup and with other stakeholders in the biodiesel industry.

CHAPTER 1: Hydrogen Fuel Quality

1.1 Introduction and Overview

> *Yes, my friends, I believe that water will one day be employed as fuel, that hydrogen and oxygen which constitute it, used singly or together, will furnish an inexhaustible source of heat and light, of an intensity of which coal is not capable. … I believe, then, that when the deposits of coal are exhausted we shall heat and warm ourselves with water. Water will be the coal of the future.*
>
> Cyrus Harding, in *The Mysterious Island* by Jules Verne, 1874

Hydrogen fuel cells, which use the electrochemical reaction of oxygen and hydrogen to generate electricity, will play an essential role in reaching California's goals for clean air and a sustainable energy supply. Much more energy efficient than conventional combustion engines, fuel cells produce only water and a small amount of heat as by-products at the point of use.

One important application of fuel cells is in the transportation sector. Applications of fuel cell technology in both automobiles and heavy-duty vehicles can help achieve the state's air quality and energy goals. Vehicles powered by fuel cell electric vehicles (FCEVs) produce no emissions of particulates, carbon dioxide, or the potent greenhouse gas (GHG) nitrous oxide (NOx). Expanded use of hydrogen as a transportation fuel will also reduce the state's dependence on petroleum, and so help to meet mandated alternative fuel use goals.

Under its Clean Transportation Program, the California Energy Commission (CEC) supports the development of alternative and renewable fuels and advanced transportation technologies to help implement the state's climate change and clean air policies. The State has set the following goals:

- A reduction in GHG emissions to 80 percent below 1990 levels by 2050.[1]
- A decrease in petroleum fuels usage to 15 percent below 2003 levels by 2020.[2]
- An increase in the use of alternative transportation fuels to 20 percent of all fuel consumed by 2020 and 30 percent by 2030.[3]
- A reduction of emissions of NO_x to 80 percent of 2010 levels by 2023 to meet current Federal ozone standards.[4]

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[1] ARB Climate Change Programs on the ARB Website: http://www.arb.ca.gov/cc/cc.htm, accessed Jan 9, 2020; California Office of the Governor, Arnold Schwarzenegger Executive Order S-3-05, June 1, 2005.

[2] *Reducing California's Petroleum Dependence*, ARB and CEC joint agency report publication #P600-03-005, 2003.

[3] California Energy Commission 2003 Integrated Energy Policy Report

[4] *Vision for Clean Air: A Framework for Air Quality and Climate Planning*, Public Review Draft CARB, the South Coast Air Quality Management District and the San Joaquin Valley Unified Air Pollution Control District, page 10,

FCEVs are a proven technology in use around the world. In California, a limited number of fuel cell passenger cars are currently leased to consumers by manufacturers in demonstration programs. Growing numbers of transit systems are using fuel cell buses. Increasingly, fuel cell forklifts and similar vehicles are in use in industrial and warehouse settings. In response to mandates to increase vehicle fuel efficiency and decrease tailpipe emissions, many major automakers plan to begin commercial sale of FCEVs in California in 2015.

To support wider use of FCEVs, a greatly expanded hydrogen infrastructure is needed. Consumer acceptance of FCEVs will largely depend on the establishment of a convenient and reliable distribution system that delivers consistently high-quality fuel. Quality specifications for hydrogen fuel and test methods to enforce compliance with these standards are needed. The work reported in this volume was undertaken to:

- Evaluate available test methods for assessing hydrogen fuel purity
- Validate existing methods that are adequate for the analysis of hydrogen fuel
- Identify areas in which further work is needed to develop adequate analytical methods

Properties of Hydrogen

Hydrogen is the most abundant element in the universe and is thought to account for 90 percent of its known mass.[5] Molecular hydrogen (two hydrogen atoms joined by a chemical bond) is too light to be retained in the earth's atmosphere by its gravitational force. So, on earth, hydrogen occurs naturally only primarily in combination with heavier elements. Bound to oxygen to form water, hydrogen comprises almost eleven percent of the mass of the oceans.[6] Smaller quantities of hydrogen are found in minerals and various other hydrides, and account for 0.14 percent of the mass of the earth's crust.[7]

In fuel cells, molecular hydrogen is an energy carrier, not a fuel or direct energy source. A fuel cell releases the chemical energy stored in the hydrogen molecule and converts it to electricity. Hydrogen has the highest energy content per unit weight mass of any element. One kilogram of hydrogen has approximately the same energy content as one gallon of gasoline. However, since hydrogen is also the lightest element, it has a low energy density by volume at standard temperature and atmospheric pressure.[8] Therefore, a given volume of hydrogen contains only a small amount of energy under ambient conditions. Hydrogen tanks in FCEVs are highly

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June 27, 2012. http://www.arb.ca.gov/planning/vision/docs/vision_for_clean_air_public_review_draft.pdf, accessed Jan 23, 2020.

[5] Hydrogen fact sheet from the Los Alamos National Laboratory Website: https://periodic.lanl.gov/1.shtml, accessed Jan 23, 2020.

[6] *Abundance of the Chemical Elements* on the ChemEurope website: http://www.chemeurope.com/en/encyclopedia/Abundance_of_the_chemical_elements.html, accessed Jan 10, 2020.

[7] Steven Dutch, Department of Natural and Applied Sciences, University of Wisconsin - Green Bay. "What the Earth is Made Of" Webpage: https://stevedutch.net/Planets/Geochem.htm, accessed Jan 10, 2020.

[8] Elert, Glenn, editor. *The Physics Factbook*™, entries 187 and 190, available on The Physics Factbook Website: http://hypertextbook.com/facts/index-topics.shtml, accessed Jan 10, 2020.

pressurized to increase the fuel density so that a FCEV can achieve an acceptable driving range of at least 300 miles.

Safety Considerations for Hydrogen

Hydrogen does have unique characteristics that require special handling precautions for safety. However, this does not mean that hydrogen is less safe than other transportation fuels. In fact, overall, hydrogen may be safer than conventional fuels. Hydrogen has long been an industrial commodity in many industries with an excellent safety record. A 1997 report on hydrogen vehicle safety prepared for the U.S. Department of Energy (DOE) concluded, "Overall, we judge the safety of a hydrogen FCEV system to be potentially better than the demonstrated safety record of gasoline or propane, and equal to or better than that of natural gas."[9]

Vapors of all transportation fuels are flammable within some range of concentrations in air. For hydrogen, this range is roughly 4 – 75 percent, quite wide compared to that of conventional petroleum fuels. However, even lower concentrations of gasoline (1 percent), diesel (0.6 percent), and propane (2.2 percent) will support combustion. In the event of a leak, both petroleum-based fuels and hydrogen can burn if an ignition source is present. In the event of a leak, hydrogen will rapidly diffuse upwards because of its lighter-than-air buoyancy. This will be true even if the hydrogen has been ignited. Consequently, hydrogen fires remain narrow, vertical, concentrated, and dissipate quickly. This reduces the risk that surrounding objects and buildings will be ignited. Vapors of gasoline and diesel fuel, on the other hand, are heavier than air. They will spread low to the ground if there is a fuel leak, increasing the fire risk to the surroundings. In this sense, hydrogen is safer than conventional fuels.

Production of Hydrogen

Since there is no terrestrial source of molecular hydrogen, it must be manufactured using a hydrogen-rich compound as the raw material. According to the U.S. Energy Information Administration, the domestic annual production of hydrogen is about nine million metric tons. The electricity that could potentially be produced from this amount could power at least 20 million cars.[10] However, hydrogen is used today mainly as a feedstock in the petrochemical, food, electronics and metallurgical processing industries. The National Aeronautics and Space Administration's space program currently uses liquid hydrogen fuel for rocket propulsion and for fuel cells onboard spacecraft to produce power, heat, and water. The use of hydrogen in fuel cells in the transportation sector is expected to grow rapidly in the coming years.

Today, roughly 95 percent of the hydrogen produced comes from reforming of natural gas.[10] Most of the remainder is produced by electrolysis of water. A small amount is produced by gasification of coal or biomass, largely for research and development efforts. Since hydrogen must be continually contained in a closed system, its method of production determines what impurities it is likely to contain. The three major production methods used today are:

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[9] Ford Motor Company Direct-Hydrogen Fueled Proton-Exchange Membrane Fuel Cell System for Transportation Applications Hydrogen Vehicle Safety Report DOE/CE/50389-502 prepared for the U. S. Department of Energy, May 1997. https://www.osti.gov/servlets/purl/534504, accessed Jan 10, 2020.

[10] U.S. Energy Information Administration, Hydrogen Explained: http://www.eia.gov/energyexplained/index.cfm?page=hydrogen_production, accessed Jan 10, 2020.

Steam methane reforming:

High-temperature steam is combined with natural gas in the presence of a catalyst to produce hydrogen. This energy intensive process is the most common and least-expensive method of production in use today.

Production of Hydrogen by Steam Reforming of Methane

Steam-Methane Reforming Reaction:

$$\mathrm{CH_4 + H_2O} \overset{catalyst}{-} \mathrm{CO + 3\,H_2}$$

Water-Gas Shift Reaction

$$\mathrm{CO + H_2O \rightarrow CO_2 + H_2 + heat}$$

Electrolysis:

An electric circuit with two electrodes immersed in water is used to split the water into its constituent elements hydrogen and oxygen. This process is the reverse of that which occurs in a fuel cell. Electrolysis is a more expensive process than steam reforming, but it can be scaled down in size easily. Electrolysis units can be powered by solar or wind energy for zero-carbon and off-the-grid applications.

Production of Hydrogen by Electrolysis

A voltage applied across two electrodes drives the reactions:

Oxidation: $\mathrm{2\,H_2O(l) \rightarrow O_2(g) + 4\,H + (aq) + 4e-}$

Reduction: $\mathrm{2\,H + (aq) + 2e- \rightarrow H_2(g)}$

The overall reaction is: $\mathrm{2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g) + heat}$

Gasification:

Heat is applied to coal or biomass in a controlled oxygen environment to produce a gas that is further separated using steam to produce hydrogen. In the 19th century, early gasification technology with coal and coke was used for gas lighting for streets, homes, and businesses.

Production of Hydrogen by Gasification:

$$\mathrm{3C\,(coal) + O_2 + H_2O \rightarrow H_2 + 3CO}$$

Water-Gas Shift Reaction:

$$\mathrm{CO + H_2O \rightarrow CO_2 + H_2 + heat}$$

Introduction to Fuel Cell Vehicles

Historical Background

The first recorded observation of hydrogen is in a paper published in 1671 by the English scientist Robert Boyle. Boyle observed that the action of an acid on iron filings produced a flammable gas. The nature of this gas was not understood until a century later, when, in 1776, Henry Cavendish published a description of its properties. Cavendish recognized that the unnamed gas was the simplest and lightest of the chemical elements and noted that water was produced when hydrogen was burned. In 1783, the French chemist Lavoisier named this element hydrogen from the Greek words hydro (water) and genes (generator). In today's fuel cells, the energy released when hydrogen reacts with oxygen to produce water is efficiently converted to electricity. FCEVs are among the many applications of fuel cell technology.

Chemists began the study of the electrochemical reactions underlying today's fuel cell technology early in the nineteenth century. In 1839, the Welsh scientist William Robert Grove was the first to publish a design for what he termed a *gas battery,* using a sulfuric acid electrolyte solution to connect electrodes sealed in bottles of hydrogen and oxygen. The term *fuel cell* was introduced by the British industrial scientists Charles Langer and Ludwig Mond, who in the late nineteenth century attempted to develop a design that would run on coal gas and air.

A practical fuel cell was not developed for nearly 60 years. In 1955, W. Thomas Grubb, working at the General Electric Company developed a fuel cell with a polymeric ion-exchange membrane. Another General Electric scientist, Leonard Niedrach, developed a method for binding a platinum catalyst to the membrane. The *Grubb-Niedrach fuel cell* was used in NASA's Gemini space program.[11] The design of fuel cells used in today's vehicles is based on the Grubb-Niedrach fuel cell*.*

Fuel Cell Vehicles

A tractor built in 1959 by the Milwaukee-based Allis-Chalmers Company is recognized as the first land fuel cell vehicle. Engineer Harry Karl Ihrig assembled 1,008 individual fuel cells with a total output of 15 kW of electricity.[12] [13] Ihrig's tractor, able to pull 3000 pounds, was demonstrated throughout the country. It was later donated to the Smithsonian.

Ihrig used the alkali fuel cell design of British engineer Francis Thomas Bacon. Bacon used potassium hydroxide as an electrolyte instead of the more corrosive sulfuric acid. Bacon's highly efficient alkaline fuel cell design was used by NASA in the Apollo and space shuttle programs. The first documented fuel cell car was the General Motors Electrovan, built in 1967.[13] The Electrovan also used an alkaline fuel cell based on the design of the Austrian inventor Karl Kordesch.

In spite of these early successes, alkaline fuel cells are considered impractical for widespread use in land vehicles because the catalyst in alkaline fuel cells is extremely sensitive to poisoning by CO_2, and so requires not only extremely pure hydrogen, but highly pure oxygen as well.[14]

Automobile manufacturers have turned instead to proton exchange membrane fuel cells of the type first developed at General Electric. (These are also called polymeric electrolyte membrane

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[11] History of fuel cell technology: http://www.fuelcelltoday.com/about-fuel-cells/history, accessed Jan 10, 2020.

[12] Hydrogen Cars Now Blogpost: http://www.hydrogencarsnow.com/blog2/index.php/fuel-cells/allis-chalmers-farm-tractor-was-first-fuel-cell-vehicle/, accessed Jan 10, 2020.

[13] History of hydrogen fueled cars: http://www.hydrogencarsnow.com/hydrogencars1807-1986.htm, accessed Jan 10, 2020.

[14] U.S. Department of Energy, Fuel Cell Types: https://www.energy.gov/eere/fuelcells/types-fuel-cells, accessed Jan 10, 2020.

fuel cells.) Proton exchange membrane fuel cells operate at roughly 175 °F (80 °C), compared to a minimum of 300 °F (150 °C) for alkaline fuel cells.[15]

Proton exchange membrane fuel cells today remain the technology of choice of automobile manufacturers. Fuel cell design is rapidly evolving, with improvements continually being made in power density and catalyst loading. These and other changes are continuing to reduce manufacturing costs.

A timeline that includes other key events in the history of hydrogen and fuel cell vehicles in California is presented in Appendix A.

Hydrogen Fuel Specifications and Test Methods

The California Legislature has determined that regulation of motor vehicle fuels offered for sale in California is necessary for public safety and consumer protection. DMS has the responsibility for establishing and enforcing quality standards for gasoline, diesel fuel, and alternative engine fuels sold in California. The authority for these activities is established by the California Oil Substitution Act, as enacted in 1931 (Statutes of 1931, Chapter 609) and subsequently amended. The provisions of this legislation are found in the California Business and Professions Code (BPC), Division 5, Chapters 14 (Petroleum) and 15 (Automotive Products). Motor fuels produced and offered for sale in California are sampled and tested in the California Department of Food and Agriculture (CDFA) laboratories in Sacramento and Anaheim to verify that they meet the quality, performance, and drivability standards established in state law.

Senate Bill 76 (Statutes of 2005, Chapter 91) defined hydrogen as a motor vehicle fuel. This definition is included in BPC Division 5, Chapter 14, Section 13401. Section 13446 of this legislation made DMS responsible for enforcing quality standards for hydrogen fuel in California. This required CDFA, with the concurrence of ARB, to adopt standards by regulation for hydrogen fuel used in both fuel cells and internal combustion engines, until an organization typically accredited by the American National Standards Institute (ANSI) formally adopts standards. When this law was enacted, only a handful of standards applying to hydrogen had been promulgated. These were not applicable to the very high purity requirements of fuel cell applications. The Compressed Gas Association's *Standard G5.3* established specifications for lower purity hydrogen gas for industrial applications such as welding. A US Department of Defense standard, *MIL-PRF-27201D*, was developed for hydrogen used as a propellant; however, this standard did not include all of the contaminants relevant to hydrogen used as fuel for FCEV. *Technical Information Report J2719* from SAE International, an ANSI-accredited standards developer, did provide specifications specifically for hydrogen for fuel cells; however, this document was advisory only and could not serve as a basis for regulation in California. To comply with Section 13446, the Department adopted regulations in California Code of Regulations (CCR) Title 4, Division 9, Chapter 6, Article 8, Section 4181 establishing interim standards for hydrogen fuel. These interim standards were developed by DMS working with the Fuel Cell Standards Committee of SAE and conformed closely to the advisory specifications of *Technical Information Report J2719*. This development work was funded in part by an interagency agreement between CDFA DMS and ARB (Agreement Number 05-612).

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[15] U.S. Department of Energy, Hydrogen and Fuel Cells Report PDF: www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf, accessed Jan 10, 2020.

In September 2011, SAE published its *Surface Vehicle Standard J2719 - "Hydrogen Fuel Quality for Fuel Cell Vehicles"* specification for hydrogen. This specification, shown in Table 1 below, is equivalent to the interim California standard. The Department has adopted the SAE International standard as a replacement for its interim standard.

Table 1: *SAE J2719* Specifications for Hydrogen Fuel

Constituent	**Chemical Formula**	**Limits**	**Laboratory Test Methods to Consider and Under Development**	**Current Detection Limit (Units are µmol/mol unless otherwise specified)**
Hydrogen fuel index	H_2	> 99.97%	Total allowable non-hydrogen, non-particulate constituents listed below	300
Water	H_20	5	No standardized test method available - ASTM test methods under development	0.5
Total hydrocarbons* (THC)	(C1 basis)	2	No standardized test method available - ASTM D1946 under revision	0.05
Oxygen	O_2	5	No standardized test method available - ASTM D1946 under revision	5
Helium	He	300	No standardized test method available - ASTM D1946 under revision	25
Nitrogen, Argon	N_2, Ar	100	No standardized test method available - ASTM D1946 under revision	11
Carbon dioxide	CO_2	2	No standardized test method available - ASTM D1946 under revision	0.01
Carbon monoxide	CO	0.2	No standardized test method available - ASTM D1946 under revision	0.02
Total sulfur	S	0.004	No standardized test method available - ASTM developing a new standard	0.004
Formaldehyde	HCHO	0.01	No standardized test method available - ASTM developing new standards	0.01

Constituent	Chemical Formula	Limits	Laboratory Test Methods to Consider and Under Development	Current Detection Limit (Units are µmol/mol unless otherwise specified)
Formic acid	HCOOH	0.2	No standardized test method available - ASTM developing new standards	0.2
Ammonia	NH_3	0.1	No standardized test method available - ASTM developing new standards	0.14
Total halogenates		0.05	No standardized test method available - ASTM developing new standard	0.01
Max. Particulate Size	na	< 10 µm	No standardized test method available ASTM developing new standard	1 µm
Particulate Concentration	na	1 µg/l	No standardized test method available - ASTM developing new standard	1 µg/l

**SAE J2719* does not include a separate specification for methane. Up to 100 µmol/mol of methane is allowed if no other hydrocarbon is present. If any other hydrocarbon is present, the combined THC limit of 2 µmol/mol applies.

Source: SAE Surface Vehicle Standard J2719 - "Hydrogen Fuel Quality for Fuel Cell Vehicles" 2011

As indicated in Table 1, few standardized laboratory test methods from an ANSI-accredited organization currently exist for establishing compliance with the specifications in *SAE J2719*. A footnote to the table in *SAE J2719* observes that, "Approved, standard test methods are not available for detecting many of the non-hydrogen constituents at the levels cited." ASTM *D1946-90 Standard Practice for Analysis of Reformed Gas by Gas Chromatography* applies to the compositional analysis of mixtures of hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, methane, ethane, and ethylene. It was not developed for the determination of ultra-trace levels of these gases as impurities, and it does not include all of the contaminants of interest for hydrogen fuel. No current ASTM method applies to the ultra-trace analysis of impurities in hydrogen.

There are some independent laboratories that can perform hydrogen analysis at the levels cited using non-standardized test methods and procedures. Standards development organizations such as ASTM are in the process of developing consensus-based test methods to analyze for non-hydrogen constituents at the low concentrations specified in Table 1. Several test methods are under development by ASTM working groups. Other test methods have been adopted by ASTM. However, these have not undergone full interlaboratory validation to demonstrate adequate reproducibility and robustness. Without tested and approved analytical test methods, the specifications in *SAE J2719* are unenforceable by regulatory agencies. This creates a critical obstacle to the development of a viable hydrogen infrastructure. Impurities in hydrogen fuel not only reduce fuel cell efficiency and compromise safety, but also can rapidly and irreversibly degrade the fuel cell stack. All stakeholders need to have confidence in the quality, reliability, and fairness of the hydrogen marketplace. The work reported here will promote these factors by identifying a suite of test methods adequate to demonstrate compliance of a fuel sample with SAE *J2719*.

Project Objectives

The work described in this report was undertaken by DMS as a first step in the development of test methods to be adopted by ASTM International (ASTM, formerly known as the American Society for Testing and Materials) to provide a foundation for construction of a hydrogen infrastructure. The project was funded by the CEC under Contract 600-09-015 with CDFA/DMS. The project involved several steps:

- A survey of available test methods for the required analytes in hydrogen.
- A selection of the most promising of the available methods for evaluation.
- The purchase and installation of the equipment required to carry out the selected methods.
- The evaluation of the selected test methods.
- The identification of gaps in analytical capability exposed in testing.
- The development of recommendations for future work to address these gaps.
- The presentation of results and recommendations to the CEC, ASTM, and other stakeholders.

The end goal of this work is the development of a set of robust analytical methods to detect and quantify impurities in hydrogen fuel as specified in *SAE J2719*. This set of methods is intended to form a basis for the regulation of hydrogen fuel quality at some point in the future. Therefore, it was necessary to consider from the outset such factors as cost, time, complexity, and minimization of sample quantity for a complete analysis of a fuel sample. This project includes the separation, identification, and quantification of contaminants present in hydrogen samples above, at, and below the proposed reporting limits. However, it is not sufficient to develop individual methods for each analyte in isolation. The goal is a set of analyses to be run as a group for a complete determination of contaminants that may be present in a sample of hydrogen fuel. Minimizing total analysis time and conserving as much of the original sample as possible are very important for a set of methods that are applicable to regulatory enforcement.

Specification for Particulates

Particulates pose potential hazards in any liquid or gaseous fuel stream. Deposition of particles can cause plugging of small orifices, filters, or screens as well as erosion of parts and assemblies within the fuel delivery train.

SAE International published the first Technical Information Report *J2719* for hydrogen fuel in November 2005. It set an upper limit of 1 µg/L for particulate quantity, with a maximum size for all particulates of 10 µm. These specifications were adopted into California Code of Regulations (CCR Title 4, Division 9, Chapter 6, Article 8, Section 4181) in September 2008.

In January 2010, CDFA/DMS chemist John Mough attended a joint SAE/International Organization for Standardization (ISO) meeting in San Francisco, California. Official representatives of both the SAE Fuel Cell Standard Committee and ISO Technical Committee 197 Working Group 12 were present, along with representatives of FCEV manufacturers. Data[16] from analytical work done on hydrogen fuel samples collected in California was presented and discussed. This data showed that in 68 sampling events, all samples passed the particulate quantity specification. However, every sample failed the particulate size requirement. Based on these results, a change in the particulate quantity specification from 1 µg/L to 1 mg/kg was adopted by the SAE and ISO representatives present. This change was consistent with the method of sale for hydrogen (by the kg rather than the L). It also lowered the quantity specification by a factor of 11 (11 µg/L = 1 mg/kg).

Although the data supported lowering the specification to 0.1 mg/kg, all parties agreed that there was no technical rationale for this level. It was also agreed that the fuel delivery systems and nozzles would be exposed to uncontrollable environmental variables that could lead to particulate contamination. Therefore, it was agreed that the particulate size requirement would best be controlled by the automotive manufacturers with appropriate filters on board the vehicle.

This was the status when the contract between the CEC and DMS covering the work reported here was signed in June 2010. Three months later, in September 2010, ASTM published test method *ASTM D7650-10 Standard Test Method for Sampling of Particulate Matter in High Pressure Hydrogen used as a Gaseous Fuel with an In-Stream Filter*, reflecting the consensus reached at the January 2010 SAE/ISO meeting. A year later, in September 2011, SAE published *Surface Vehicle Standard J2719 – Hydrogen Fuel Quality for Fuel Cell Vehicles*. With a consensus method in place, it was not necessary for DMS to develop a method for the determination of particulates in hydrogen fuel. This document is from an ANSI-accredited Standards Development Organization, and so has been adopted as the particulate specification for hydrogen in California. In light of these developments, no work on particulates was performed by DMS under this contract.

More recently, particulates have been found in some hydrogen fuel samples in California. Such particulates have caused performance problems in vehicles without filters. Depending on measures taken by hydrogen industry and vehicle manufacturers, future work to validate *ASTM D7650-10* may be necessary.

1.2 Analysis of Hydrogen Fuel Quality

Challenges in Hydrogen Fuel Analysis

Many well-established standard test methods exist for the analytes specified in *SAE J2719*. However, there are several challenges to their application to hydrogen fuel analysis:

- The very low concentrations that must be reliably detected (less than 20 parts per billion for most of the contaminants).

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[16] The data on particulates in hydrogen fuel samples discussed at this meeting is confidential business information and is proprietary.

- The physical characteristics of the hydrogen matrix, a high pressure, flammable gas that is incompatible with many common materials.
- The need to draw a representative sample from storage tanks and dispensers.
- The need to deliver the required quantity of sample to an analyzer without changing its composition.

Survey of Existing Methods for the Analysis of Contaminants in Hydrogen

The complex matrix of impurities listed in *SAE J2719* precludes the use of any single instrument or method for hydrogen fuel quality analysis. The chemical contaminants vary widely in physical and chemical properties. The maximum contamination levels range over approximately five orders of magnitude. No one analytical technique can cover this range of testing for all of the *SAE J2719* analytes. The goal of the survey of existing test methods was to identify a minimum number of methods that apply to all the analytes and:

- Have sufficient sensitivity.
- Require minimum analysis times.
- Use readily available and affordable laboratory equipment and apparatus.
- Do not require exceptional expertise to perform.
- To the extent possible, provide secondary methods for confirmation of findings.

These goals were formulated to provide gas suppliers, station operators, and regulators with analytical methods that are fast, inexpensive, and reliable to ensure that hydrogen fuel offered for sale meets the specifications of *SAE J2719*.

Working groups of ASTM and the ISO have identified a suite of analytical methods with potential application to the analysis of impurities in hydrogen fuel. Based on these lists and the criteria given above, the following methods were considered for evaluation in this project:

- Gas Chromatography-Mass Spectrometry (GC-MS) for the analysis of oxygen, nitrogen, argon, carbon monoxide, carbon dioxide, hydrocarbons, and halogenates.
- GC-Pulsed Discharge Helium Ionization Detector (GC-PDHID) for the analysis of argon, oxygen, nitrogen, carbon dioxide, carbon monoxide.
- GC-Flame Ionization Detector (GC-FID) with methanizer for the analysis of methane, ethane, THC, CO, and CO_2.
- GC-Thermal Conductivity Detector (GC-TCD) for the analysis of helium.
- GC- Electron Capture Detector (GC-ECD) for the analysis of oxygen and halogenates.
- GC-Pulsed Flame Photometric Detector (GC-PFPD) for the analysis of sulfur compounds.
- Ion Chromatography (IC) for the analysis of ammonia.
- Fourier Transform Infrared Spectroscopy (FTIR) for the analysis of water, ammonia, formic acid, formaldehyde, hydrocarbons, carbon monoxide, and carbon dioxide.

Table 2 summarizes the matrix of possible test methods for the analytes of interest that were selected for this project. Because staff, resources, and time were limited, not every possible analytical approach could be tested.

Equipment and Apparatus Overview

Based on the analysis scheme of Table 2, the necessary equipment was ordered, following California Department of General Services Procurement Division policies and procedures. A Varian/Brucker GC-MS that the CDFA already owned was identified as a starting point.

In the first procurement step, a PFPD was added to the GC-MS system, which will be designated System 1 in this report. A second Varian GC, with PDHID, FID, and TCD detectors was purchased to cover the remaining GC analytes. This instrument is designated System 2. The PDHID was from VICI; the remaining detectors were from Varian/Bruker. In both systems, chromatographic separation of the analytes for each detector is accomplished by pairs of HayeSep N® and molecular sieve columns.

Randall Cook of Lotus Consulting provided a custom sample switching apparatus for Systems 1 and 2. With this apparatus, it is possible to direct the sample from a single injection to all detectors on a system through precise timing of a set of switching valves. This approach was chosen to minimize both the time and total amount of sample required for a complete analysis.

A Nicolet 6700 FTIR with a 10 m gas cell, liquid nitrogen-cooled mercury cadmium telluride detector, and OMNIC software, was purchased from Thermo Scientific. Finally, a Dionex IC5000 Ion Chromatograph with Chromelon software completed the initial round of equipment procurements.

After the project was underway, additional instrumentation needs are identified when sensitivity and precision requirements could not be met by the first methods tested. Problems are encountered in the determination of ammonia, water, formaldehyde, and formic acid. Other researchers have identified cavity ring down spectrometry (CRDS) as an analytical method sensitive enough to determine both ammonia and water in hydrogen fuel.[17] This emerging technology can accurately determine the concentration of a specific analyte in this gas phase by measuring the time required for decay of a characteristic frequency of light absorbed by that analyte. A tuned laser and detector calibrated for a specific absorption frequency yields a timed response that is a direct function of concentration. CRDS has been successfully applied to the determination of water vapor in gaseous hydrogen samples down to 0.100 ppm. Recent advances have led to CRDS instruments capable of analyzing ammonia in hydrogen down to 0.004 ppm. A CRDS gas analyzer configured for these analytes was purchased from Tiger Optics after a test of a loaner instrument demonstrated adequate sensitivity. A module for formaldehyde analysis was added later.

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[17] Andrew S. Brown et al, National Physical Laboratory *Report AS 64 Methods for the analysis of trace-level impurities in hydrogen for fuel cell applications*, August 2011.

Table 2: Analytical Options for Hydrogen Fuel Analysis

Analytes	Methanizer-FID	GC-ECD	GC-PDHID	GC-PFPD	GC-TCD	GC-MS	FTIR	IC
Water						X	X	
Hydrocarbons	X					X	X	
Oxygen		X	X			X		
Helium					X			
Nitrogen			X			X		
Argon			X			X		
Carbon dioxide	X		X			X	X	
Carbon monoxide	X		X			X	X	
Sulfur compounds				X		X	X	
Formaldehyde	X					X	X	X
Formic acid						X	X	X
Ammonia						X	X	X
Halogenates		X				X	X	

Source: ASTM and ISO

A laboratory information management system was required for sample tracking, data review, report generation, and data archiving. To meet this need, a second license was obtained for the STARLIMS® system already in place at the CDFA Center for Analytical Chemistry. A contract was signed with C&G Technology Services Inc. to customize the STARLIMS® system for this project and to create a firewall between the two programs using the CDFA STARLIMS® server. Custom software was written for DMS to allow the automatic uploading of data files from the laboratory instruments to the STARLIMS® system, to eliminate typographical and transcription errors arising from manual data entry. A barcode system was included to provide tracking of the sample containers. Tracking of a sample chain of custody was also incorporated in the customized STARLIMS® system. STARLIMS® is a web-based application, so that future expansion of the system can include sample logging in the field.

Preparation of Standards

Validated standards of the contaminants of interest in a hydrogen matrix are not commercially available at this time. Therefore, laboratory staff designed an apparatus and developed procedures to prepare the calibration and quality assurance standards required for this project. Test standards were prepared from pure neat materials and diluted with ultra high-purity hydrogen. The preparation of standards is detailed in Hydrogen Laboratory Standard Operating Procedure #3 - for Preparation of Gaseous Hydrogen Standards. The complete SOP may be found in Appendix B. A brief summary will be presented here.

Standard mixtures are prepared in six L SUMMA canisters. These canisters have electro-polished stainless steel interiors passivated with a coating of Silonite™ to reduce analyte adsorption. Canisters were obtained from either Restek (catalog # 24142), or Entech

Instruments Inc. (catalog # 29-10622G). In addition, a Model 3108 Canister Cleaner was purchased from Entech. This cleaning system uses a combination of heat and vacuum to prevent cross-contamination. Figure 59 in Appendix C shows SUMMA canisters in the cleaning oven.

Figure 1 illustrates the valve and meter assembly used to introduce hydrogen and analytes into the canisters. The unit consists of a pressure gauge, a septum-equipped introduction tee, an isolation valve, a hydrogen introduction valve, and an evacuation valve. This apparatus allows for the evacuation of the standards preparation assembly, the introduction into the standards container of an aliquot of neat material, using gas tight syringes, and dilution with ultra high purity hydrogen.

The maximum working pressure for the SUMMA canisters is 40 psig. A pressure differential between the canister and the inlet of the GC is required for the flow of sample to the instrument. These considerations limit the volume of standard that can be prepared at one time to about 16 useable liters (L): 40 psi / 14.7 psi x 6L = 16.3 L (1 atm ~ 14.7 psi).

All standards that are purchased or prepared in the laboratory are assigned an S-XXX or SHS-XXX number, respectively, to ensure traceability. An identification system and spreadsheet were developed to track and record standards receiving and preparation. The numbering system for neat standards is S-XXX, where S stands for Sacramento and XXX is a sequential number. The numbering system for laboratory prepared standards is SHS-XXX, where SHS stands for Sacramento Hydrogen Standard, and XXX is a sequential number. These numbers are included in the final laboratory analysis reports to document the standards used for calibration. Examples of these analytical reports are included in the discussion below.

Most of the standards prepared are in the low- to mid-ppm range. The required volume of an analyte is found using an Excel 'Standard Prep Template' that calculates the volume required based on the target concentration and pressure of the standard.

This spreadsheet calculates the volume of neat material necessary to produce a given final volume and pressure. All standards that are received or prepared are assigned an S-XXX or SHS-XXX number to ensure traceability. An example of the spreadsheet is found in Appendix B.

Figure 1: Standards Preparation Apparatus

Photo Credit: DMS Hydrogen Laboratory

Sampling Apparatus and Method

Collecting a representative hydrogen fuel sample from a dispenser and maintaining it with no change in composition throughout collection, transport, storage, and analysis poses a significant challenge. A gaseous sample such as hydrogen fuel is homogenized through rapid diffusion of the components within a container. However, trace impurities may be adsorbed on the surfaces of the sampling interface, causing them to be under-determined. Avoiding contamination through the sampling process itself is also a challenge.

ASTM began the development of a test method for the sampling of high-pressure hydrogen fuel in 2008. The method was adopted as ASTM standard *D7606-11 Standard Practice for Sampling of High Pressure Hydrogen and Related Fuel Cell Feed Gases* in September 2011. *D7606-11* gives detailed instructions for the construction of a sampling apparatus for hydrogen fuel and for the sample collection procedure. Figure 2 shows the hydrogen quality sampling apparatus used for work reported here. The hydrogen quality sampling apparatus was designed according to the specifications of *D7606-11*e.[18] A container used to collect a hydrogen fuel sample can be seen in Figure 2 the attached to the hydrogen quality sampling apparatus. These containers, from Entech Instruments Inc., were passivated before use. They are rated for pressures up to 1800 psi and are filled to roughly 1000 psi in use.

Figure 2: Hydrogen Quality Sampling Apparatus

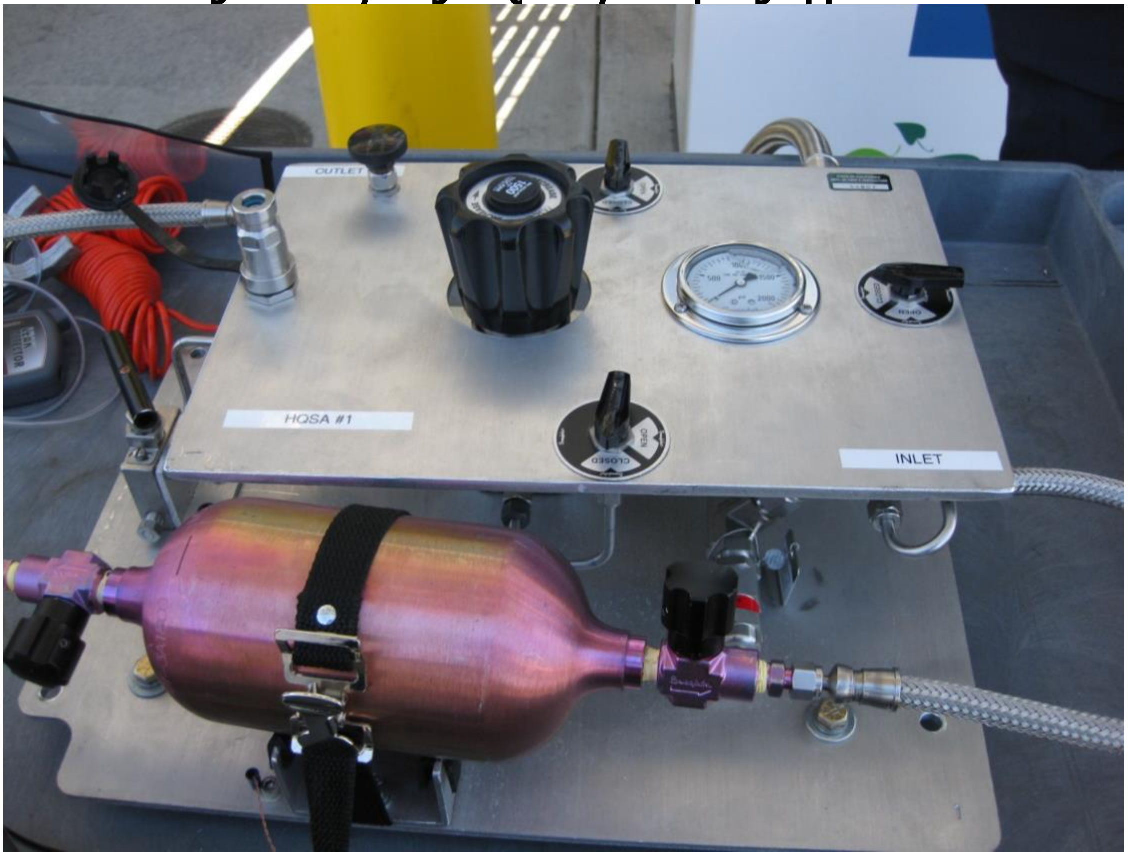

Photo Credit: DMS Hydrogen Laboratory

System 1 Instrumentation

System 1 is used for the analysis of oxygen, sulfur compounds, and halogenates. It consists of a Bruker 450 GC equipped with a multi-port auto-sampling valve and three detectors (ECD, PFPD, and a SCION SQ MS). The detectors and their target analytes are shown in Table 3. While the MS detector is able to detect all analytes except helium, for this project, it was evaluated only for those analytes listed in Table 3.

A schematic diagram of the sample flow path for System 1 is shown in Figure 3. A container of the hydrogen gas sample or calibration mixture is connected through heated stainless-steel gas lines to the GC auto-sampler. Sample introduction is controlled by the instrument software interface. Three separate sampling loops concentrate and direct the sample to the appropriate detectors through a series of carefully timed valve switching operations. The sample loops are purged for 0.95 minutes at the start of each run to sweep out any impurities and ensure that representative samples are obtained.

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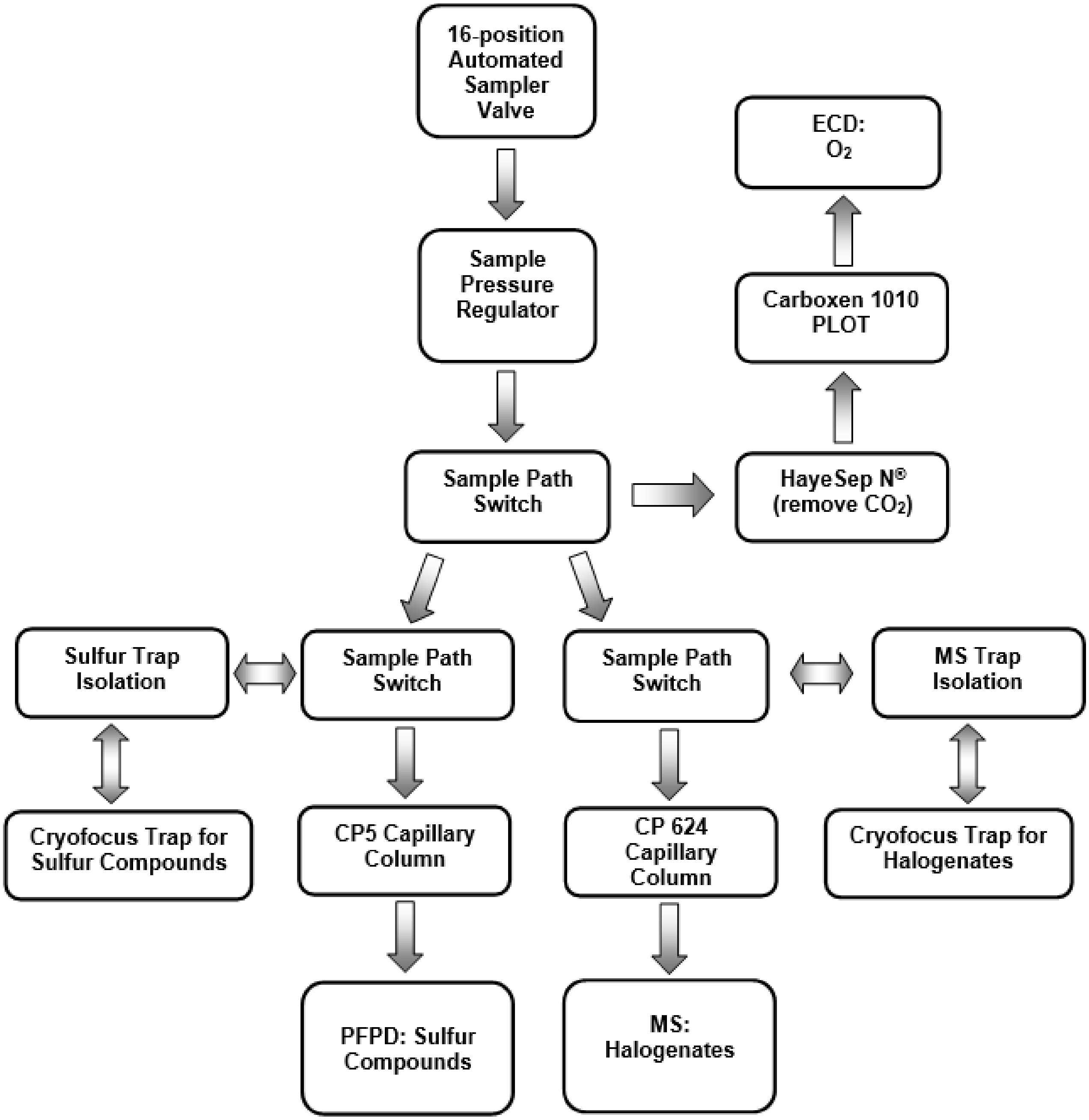
[18] ASTM publications are protected by copyright, so details of *D7606-11* may not be reproduced in this report. ASTM test methods are available for purchase from the ASTM website: www.astm.org/Standard/index.shtml, accessed Jan 10, 2020.

Figure 3: System 1 Sample Flow Path for ECD, PFPD, and Mass Spectrometer



Source: DMS Hydrogen Laboratory

Table 3: System 1 Detectors and Analytes

Detector	Analytes
ECD	O_2
PFPD	Sulfur compounds
MS	Halogenates

Source: DMS Hydrogen Laboratory

For oxygen analysis, the sample is injected onto HayeSep N® and Carboxen 1010 PLOT capillary columns connected in series. The HayeSep N® column is used to retain CO_2 and heavier compounds from entering and contaminating the PLOT column. A valve is mounted between the two columns and is switched to back flush the CO_2 and other impurities out of the system before the next injection.

The other two sample loops are mounted in separate cold traps held at -180° C with liquid nitrogen. These loops are purged for six minutes to concentrate the target sulfur and halogen compounds at the sample inlet. After sample concentration, one sample loop is directed to a Varian dimethyl siloxane CP5 CB capillary column connected to a PFPD for the determination of total sulfur compounds. Total sulfur content is determined by summing individual analyte peaks.

The third sample loop is directed to an Agilent CP 624 capillary column and the mass spectrometer for the determination of halogenated compounds. The total halogenates is determined by summing individual analyte peaks.

Key instrument parameters for System 1 are listed in Appendix D.

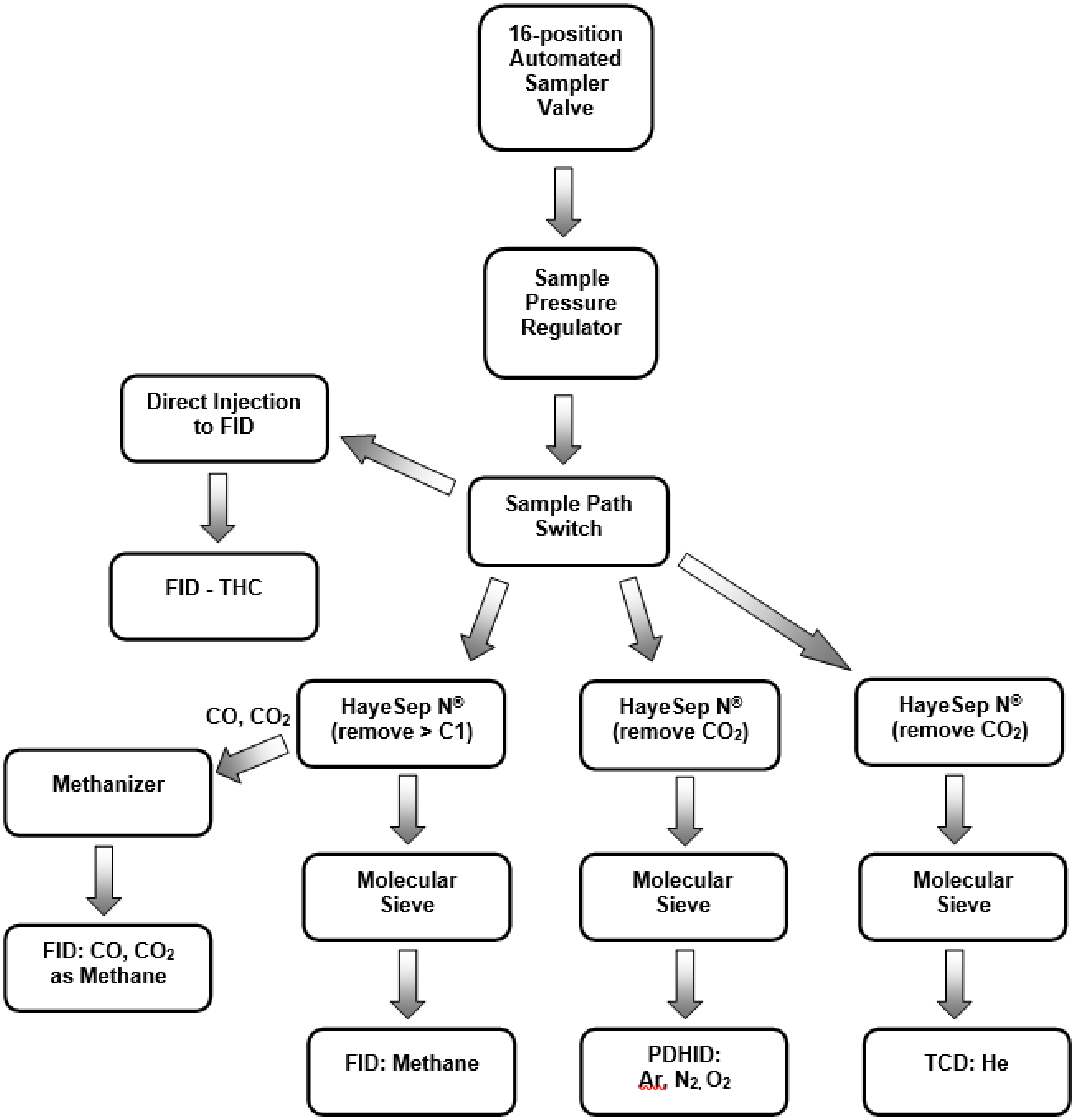
System 2 Instrumentation

System 2 is used for the analysis of He, N_2, Ar/O_2, methane, THC, CO and CO_2. It consists of a Bruker 450 GC equipped with a multi-port auto-sampling valve and 4 separate gas sampling loops serving 3 detectors. Table 4 lists the analytes seen by each of the detectors in System 2.

A schematic diagram of the sample flow path for System 2 is shown in Figure 4. The sample introduction interface is similar to that of System 1. There are four sample loops, which are purged for 0.95 minutes to sweep out any impurities and ensure a representative sample for each detector loop. A series of carefully timed valve switching operations then directs the sample from each injection loop through the desired analytical path.

Figure 4: System 2 Sample Flow Path

(PDHID, FID, and TCD)



Source: DMS Hydrogen Laboratory

Table 4: System 2 Detectors and Analytes

Detector	Analytes
FID (direct inj.)	THC
FID	Methane
Methanizer/FID	CO and CO_2 (as methane)
PDHID	Ar, N_2, O_2
TCD	He

Source: DMS Hydrogen Laboratory

One sample loop goes directly to the FID for THC determination with no chromatographic separation. *SAE J2719* requires a determination of methane separately from any other hydrocarbons that may be present. This is accomplished by the second sample loop, which also goes to the FID. Methane in a sample passes through a HayeSep N® column and a molecular sieve to the detector. The HayeSep N® column retains CO, CO_2, and any heavier hydrocarbons. CO and CO_2 are flushed from the HayeSep N® to a methanizer that converts them to methane for detection by the FID. The HayeSep N® is then isolated and back flushed to remove heavier hydrocarbons and any other contaminants from the system before the next injection.

Both of the other two sample loops also pass through a HayeSep N® column followed by a molecular sieve column. Between the two column types is a switching valve that can operate the columns in series or bypass. The HayeSep N® column is used to separate and trap CO_2 to prevent contamination of the molecular sieves. The remaining sample is separated into its components by the molecular sieve and carried forward to the individual detectors for identification and quantification.

CO_2 is detected and quantified by purging the HayeSep N® column in the FID sample loop through a methanizer in which CO_2 is converted to CH_4 and then detected by the FID. CO can also be detected by conversion to CH_4 through the methanizer; however, the sensitivity was too low to meet the reporting limit required by *SAE J2719*.

The remaining analytes in each sample loop are detected after chromatographic separation but are chemically unaltered. Key instrument settings for System 2 are listed in Appendix D.

FTIR Spectrometer

FTIR was evaluated for the analysis of hydrocarbons, carbon dioxide, carbon monoxide, ammonia, and water. FTIR was chosen as one on the starting points for this study due to its relatively short analysis times, readily available commercial instruments, and ease of operation. FTIR is based on the characteristic frequencies of vibrations of the atomic bonds within a molecule. An infrared beam passing through a sample is attenuated when the frequency of the radiation matches a characteristic vibrational frequency of an analyte. This attenuation is measured over a range of frequencies, typically 4000 to 400 cm^{-1} (equivalent to a wavelength range of 25 to 2.5 µm), to produce an infrared spectrum. The infrared spectrum of gases consists of a set of sharp peaks.

Most molecules have a characteristic infrared spectrum, which serves as a molecular fingerprint. Completely symmetrical molecules, such as oxygen and nitrogen, and monatomic species, including helium and argon, do not absorb mid-infrared radiation. With these exceptions, FTIR has the potential to be applicable the contaminants in *SAE J2719*. U.S. Environmental Protection Agency (EPA) Method 320 "***Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy***"[19] and U.S. EPA Method 8000C *"Determinative Chromatographic Separations"*[20] were used as a starting point for method development.

A Nicolet 6700 FTIR spectrometer, shown in Figure 5, was purchased for this study. It is equipped with a 10 m heated gas cell, purged optical bench, and a liquid nitrogen-cooled mercury cadmium telluride detector. Proprietary OMNIC software from Thermo-Scientific OMNIC operates the instrument and does the data collection and processing. Key instrument parameters for the FTIR are included in Appendix D.

The sample interface for the FTIR had to meet several requirements. The pressure of the hydrogen in the sample canister is much higher than is normally encountered in gas analysis. Since the extremely low levels of detection were required, adsorption of analytes on transfer lines or in the gas cell was of particular concern. An interface meeting these requirements was not commercially available, so DMS laboratory staff designed and constructed a custom interface, seen on the right in Figure 5. This interface includes:

- An oven to heat the sample containers.
- Heated transfer lines to a multi-port selector valve.
- A heated pressure regulator to reduce the incoming sample pressure to avoid over-pressurizing the gas cell.
- Temperature controllers for the heated lines and regulator.
- Pressure transducer and read-out to monitor the gas cell pressure.
- Rotameter for visual indication of flow.
- Associated electronics for monitoring and control.

Key instrument settings for System 2 are listed in Appendix D.

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[19] U.S. EPA Method 320 "*Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive Fourier Transform Infrared (FTIR) Spectroscopy*", PDF Version: https://www.epa.gov/sites/production/files/2019-06/documents/method_320.pdf, accessed Jan 10, 2020.

[20] U.S. EPA Method 8000C *"Determinative Chromatographic Separations"*, PDF Version: http://www.caslab.com/EPA-Methods/PDF/EPA-Method-8000C.pdf, accessed Jan 10, 2020.

Figure 5: Nicolet FTIR with Heated Gas Cell and Sample Interface

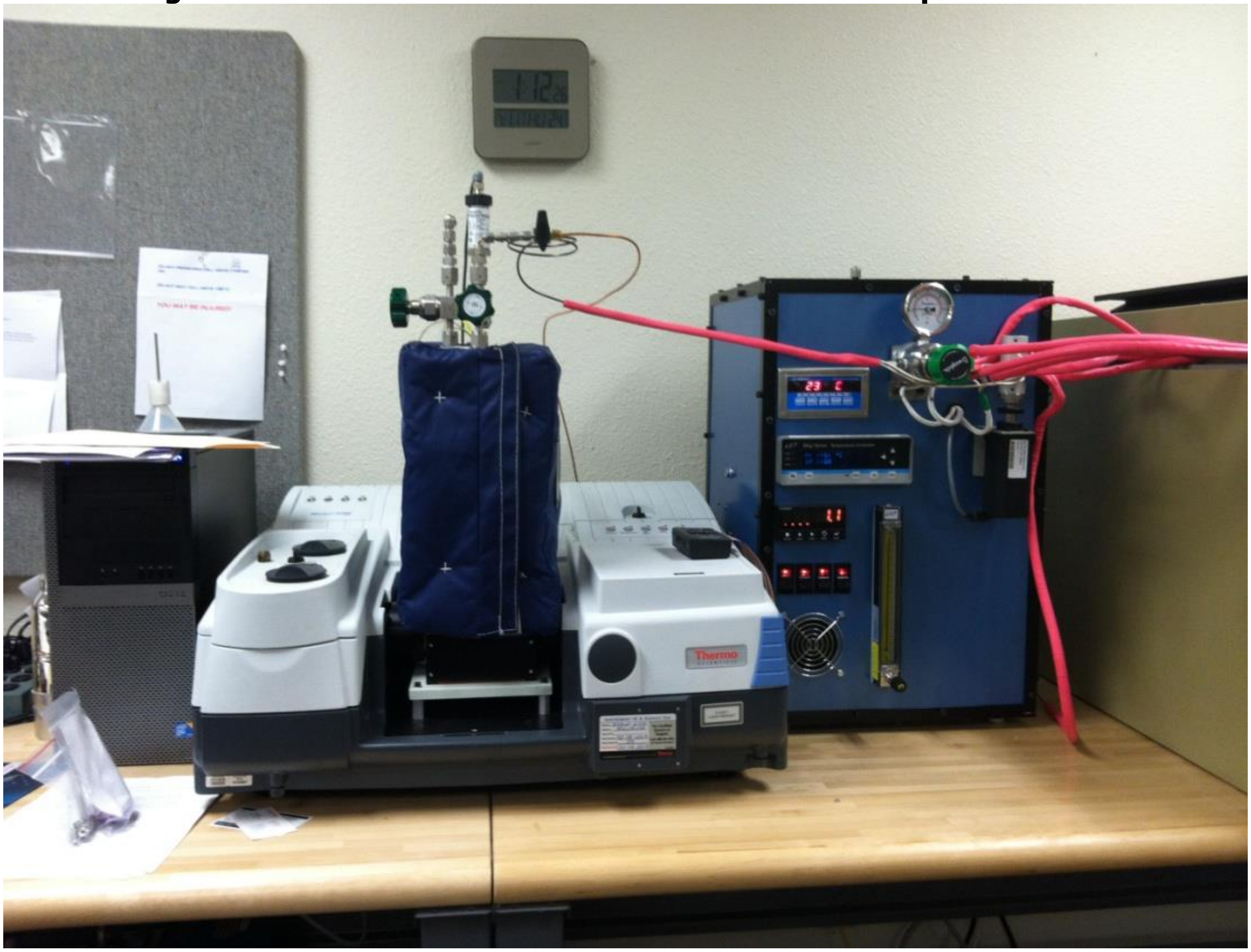

Photo Credit: DMS Hydrogen Laboratory

Cavity Ring Down Spectrometer:

CRDS was evaluated for the analysis of water and ammonia. It may also be applicable to the analysis of formaldehyde and oxygen. CRDS is an emerging technology that can accurately determine the concentration of a specific analyte based on the time required for the decay, or ring down, of an optical signal due to absorption of a molecule’s characteristic absorption frequency. A tuned laser and detector calibrated for the specific frequency yields a timed response that is a direct function of concentration. This technology has been demonstrated to be applicable to trace analysis in gas samples. It can be used for the determination of water (H_2O) vapor in gaseous hydrogen down to 0.100 ppm. Recent innovations have produced CRDS instruments capable of analyzing ammonia in hydrogen down to 0.004 ppm. A CRDS instrument with modules for ammonia and water analysis was brought to the DMS Hydrogen Laboratory for evaluation. Proof-of-concept experiments established that CRDS is a viable method for the quantitative determination of ammonia in hydrogen fuel samples. Based on this testing, a Tiger Optics Laser Trace 3X CRDS system for ammonia was purchased. A CRDS module for the determination of formaldehyde was added later.

Key instrument settings for the CRDS are included in Appendix D.

1.3 Results and Discussion

System 1: Determination of oxygen, sulfur compounds, and halogenates

Halogenates

EPA Method TO-15 was used as a guide in developing this analysis.[21] A commercial calibration mixture of halogenated and aromatic standards in nitrogen[22] was used to identify compounds that could be detected with sufficient sensitivity. Although this calibration mixture included aromatic hydrocarbons, these were not included in the GC/MS analysis as part of this project. If present in a hydrogen fuel sample, aromatics would be observed in the GC/MS chromatogram and could be identified by their mass spectrum. The halogenated compounds in this mixture are shown in Table 5. The nominal concentration for all analytes in the mixture was 1.00 ppm; the NIST traceable certified concentrations ranged from 0.96 to 1.06 ppm. Calibrations were determined over the range 2.5 – 30.0 ppb. This range was chosen to ensure that individual and total analyte concentrations could be determined with the required sensitivity. For most analytes, values of the correlation coefficient (R_2) was greater than 0.9. Method detection limits were not generated for these compounds because of the time required. These can be done in the future for specific compounds that are detected in field samples.

Table 5: Halogenates Tested by GC/MS

Halogenates	Halogenates	Halogenates
Freon-12	1,1-Dichloroethane	1,2,4-Trichlorobenzene
Chloromethane	1,1,1-Trichloroethane	Hexachloro-1,3-butadiene
Freon-114	Carbon tetrachloride	cis-1,2- Dichloroethene
Vinyl chloride	1,2,-Dichloropropane	Chloroform
Bromomethane	Trichloroethylene	1,2-Dichloroethane
Chloroethane	Chlorobenzene	trans-1,2-Dichlorpropene
Freon-11	1,1,2,2-Tetrachloroethane	cis-1,2-Dichlorpropene
1,1-Dichloroethene	1,2-Dichlorobenzene	1,1,2-Trichloroethane
Methylene chloride	1,3-Dichlorobenzene	Tetrachloroethane
Freon-113	1,4-Dichlorobenzene	1,2-Dibromoethane

Source: DMS Hydrogen Laboratory

A representative chromatogram of the standards mixture is shown in Figure 6. For clarity, not all peaks are labeled.

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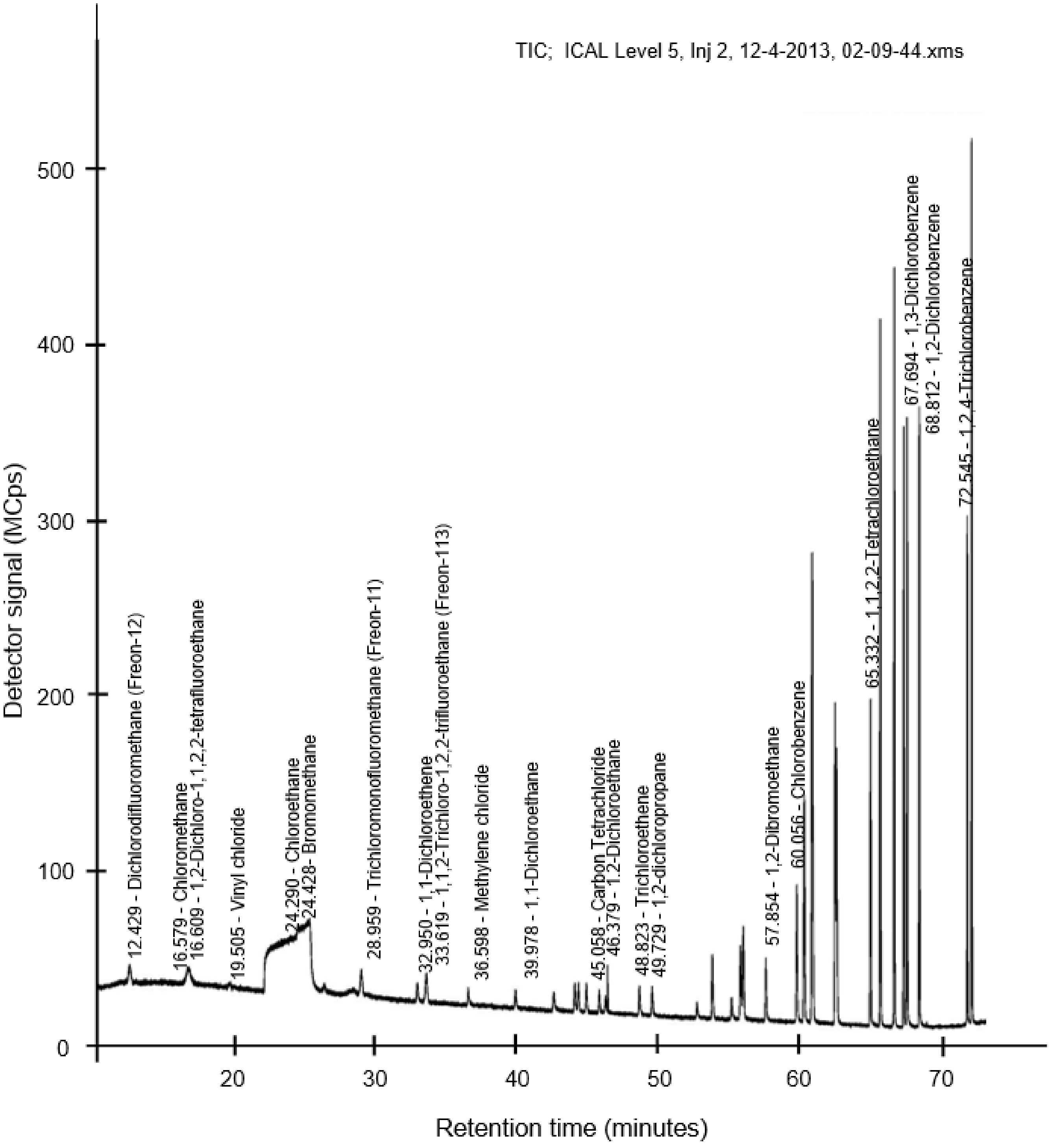
[21] EPA Method TO-15: http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-15r.pdf, accessed Jan 10, 2020.

[22] Restek TO-14A Calibration Mix Catalog #34400

Figure 6: GC/MS Chromatogram of Halogenated Standards



Source: DMS Hydrogen Laboratory

Sulfur Compounds

Dynacal Permeation tubes from VICI Metronics, Inc. were used to generate calibration mixtures of eight sulfur compounds. The compounds tested are shown in Table 6. The permeation rates of seven of these tubes were certified traceable to NIST standards. The exception was the methyl ethyl mercaptan tube, for which certification was not available. The seven certified tubes were assigned unique DMS identification codes for tracking. Because of the high sensitivity of the PFPD detector, the high permeation rate hydrogen sulfide tube S-891 was not needed for the preparation of standard mixtures.

Table 6: Sulfur Compounds Tested

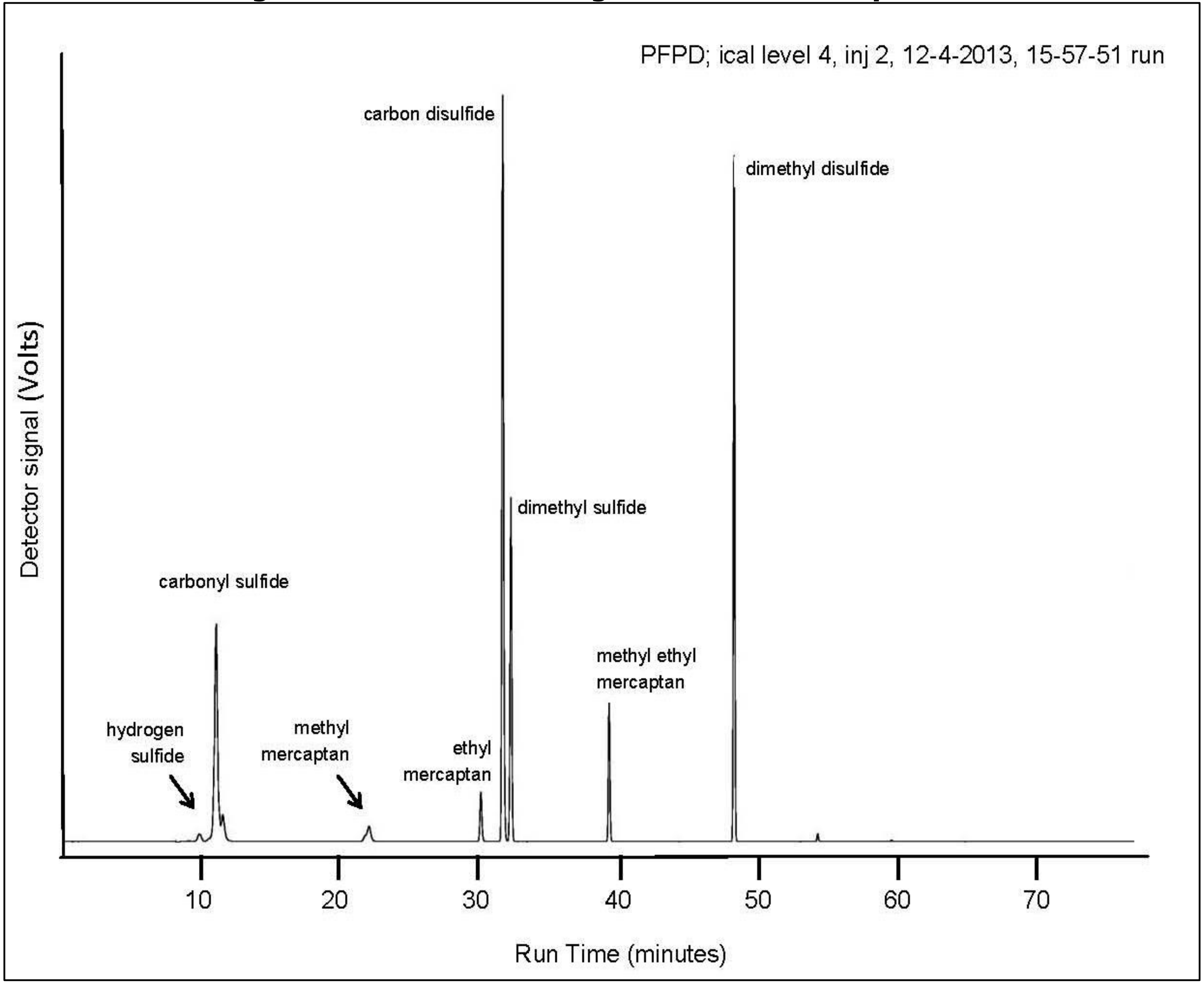
Compound	DMS ID	Serial Number	Permeation Rate (ng/min)
Hydrogen sulfide	S-890	56-38530	20.85
Hydrogen sulfide	S-891*	F-36917	1,568.94
Methyl mercaptan	S-892	T-38221	38.89
Carbonyl sulfide	S-893	F-37123	118.89
Dimethyl sulfide	S-894	33-38529	87.04
Carbon disulfide	S-895	T-37133	29.43
Dimethyl disulfide	S-896	89-37137	30.86
Ethyl mercaptan	S-897	33-38528	29.74
Methyl ethyl mercaptan	NA	NA	34.00

* This tube was not used in the calibration.

Source: DMS Hydrogen Laboratory

To generate a calibration, the eight permeation tubes were connected in series to the System 1 sulfur cryotrap inlet. The trap was loaded at a flow rate of 50.0 ml/min for times ranging from 0.5 to 6.0 minutes to obtain a series of five concentration levels to generate calibration curves. Table 7 shows the concentrations for each analyte in ppm for the five calibration levels based on the indicated flow time through the permeation tubes. Figure 7 shows the PFPD chromatogram for the Level 4 calibration mixture (analyte retention times are listed in Table 12). The PFPD has a second-order response to sulfur concentration, so quadratic calibration curves (analyte concentration = $A*Y_2 + B*Y + C$) are generated. Table 9 lists the coefficients of the quadratic calibration equation obtained for each compound.

Figure 7: PFPD Chromatogram of Sulfur Compounds



Source: DMS Hydrogen Laboratory

Table 7: Sulfur Compound Calibration Mixtures (Concentrations in ppm)

Compound	Level 1: 6 minutes	Level 2: 3 minutes	Level 3: 2 minutes	Level 4: 1 minute	Level 5: 0.5 minute
Hydrogen sulfide	0.0626	0.0313	0.0209	0.0104	0.0052
Carbonyl sulfide	0.2025	0.1012	0.0675	0.0337	0.0169
Methyl mercaptan	0.0827	0.0413	0.0276	0.0138	0.0069
Ethyl mercaptan	0.0490	0.0245	0.0163	0.0082	0.0041
Carbon disulfide	0.0395	0.0198	0.0132	0.0066	0.0033
Dimethyl sulfide	0.1433	0.0717	0.0478	0.0239	0.0119
Methyl ethyl mercaptan	0.0457	0.0228	0.0152	0.0076	0.0038
Dimethyl disulfide	0.0395	0.0198	0.0132	0.0066	0.0033

Source: DMS Hydrogen Laboratory

Table 8-A: Sulfur Compound Peak Areas

Compound	Level 1	Level 2	Level 3	Level 4	Level 5
Hydrogen sulfide	8,448	2,643	800	180	144
Carbonyl sulfide	367,000	251,113	82,333	41,540	15,715
Methyl mercaptan	29,301	11,770	4,833	762	323
Ethyl mercaptan	21,438	5,883	2,777	518	350
Carbon disulfide	223,994	57,542	19,344	4,916	1,365
Dimethyl sulfide	69,633	19,530	7,977	2,195	488
Methyl ethyl mercaptan	19,761	6,706	3,129	794	130
Dimethyl disulfide	97,203	21,033	9,109	1,933	417

Source: DMS Hydrogen Laboratory

Table 8-B: Response Factors from the Initial Calibration

Compound	RF1	RF2	RF3	RF4	RF5	RSD
Hydrogen sulfide	134,973.75	84,454.46	38,344.82	17,255.17	27,608.27	80.78
Carbonyl sulfide	1,812,509.35	2,480,352.38	1,219,858.31	123,0925.97	931,343.36	40.25
Methyl mercaptan	354,308.64	284,646.44	175,322.38	55,284.77	46,868.72	74.50
Ethyl mercaptan	437,770.55	240,265.34	170,121.58	63,466.32	85,765.29	75.50
Carbon disulfide	5,664,416.50	2,910,273.08	1,467,527.78	745,902.25	414,221.55	95.57
Dimethyl sulfide	485,846.93	272,531.43	166,972.60	91,890.40	40,858.78	83.33
Methyl ethyl mercaptan	432,672.03	293,659.09	205,530.71	104,308.97	34,156.59	73.35
Dimethyl disulfide	2,900,257.36	1,255,128.20	815,358.92	346,050.89	149,304.94	100.39

Source: DMS Hydrogen Laboratory

Table 9: Sulfur Compound Calibration Equation Coefficients

Analyte	A	B	C
Hydrogen sulfide	1.82E+06	2.44E+04	-8.64E+03
Carbonyl sulfide	4.28E+06	9.40E+05	-3.66E+05
Methyl mercaptan	1.65E+06	2.46E+05	-3.15E+04
Ethyl mercaptan	8.05E+06	4.61E+04	-2.15E+04
Carbon disulfide	1.46E+08	-9.17E+04	-2.24E+05
Dimethyl sulfide	3.02E+06	5.88E+04	-7.05E+04
Methyl ethyl mercaptan	5.76E+06	1.88E+05	-2.05E+04
Dimethyl disulfide	9.85E+07	-4.32E+05	-9.60E+04

Source: DMS Hydrogen Laboratory

A Method Detection Limit (MDL) study was performed using concentration Level 4. Table 10 shows the observed peak areas, and Table 11 shows the calculated concentration for each data point. Note that the peak area for MDL 1 for carbonyl sulfide appears to be an outlier, and so was omitted from the MDL calculation. Table 12 shows the retention time, calculated MDL, standard deviation, and Student t-test statistic for each analyte. The t-test value for carbonyl sulfide is based on seven and not eight data points, and so is higher than that of the other analytes.

Table 10: Sulfur Compound MDL Peak Areas

	MDL 1	**MDL 2**	**MDL 3**	**MDL 4**	**MDL 5**	**MDL 6**	**MDL 7**	**MDL 8**
Hydrogen sulfide	380	400	521	470	725	531	443	546
Carbonyl sulfide	4,989	10,732	12,544	11,207	9,105	10,761	13,053	11,214
Methyl mercaptan	882	764	1,383	1,120	1,057	1,010	1,168	1,276
Ethyl mercaptan	861	764	1,188	873	680	669	732	685
Carbon disulfide	9,015	8,401	11,274	9,601	6,545	6,562	6,428	5,937
Dimethyl sulfide	3,532	3,305	4,226	3,726	2,825	2,854	2,812	2,625
Methyl ethyl mercaptan	1,047	1,103	1,808	1,359	806	1,003	875	839
Dimethyl disulfide	3,029	3,320	4,544	3,428	2,904	2,696	2,644	2,457

Source: DMS Hydrogen Laboratory

Table 11: Sulfur Compound Measured MDL Concentrations in ppm

	MDL 1	MDL 2	MDL 3	MDL 4	MDL 5	MDL 6	MDL 7	MDL 8
Hydrogen sulfide	0.0122	0.0125	0.0141	0.0134	0.0167	0.0143	0.0131	0.0145
Carbonyl sulfide	--	0.0099	0.0117	0.0104	0.0083	0.0099	0.0121	0.0104
Methyl mercaptan	0.0118	0.0127	0.0135	0.0126	0.0124	0.0122	0.0128	0.0132
Ethyl mercaptan	0.0087	0.0082	0.0103	0.0087	0.0077	0.0076	0.0080	0.0077
Carbon disulfide	0.0086	0.0083	0.0095	0.0088	0.0075	0.0075	0.0074	0.0072
Dimethyl sulfide	0.0298	0.0289	0.0326	0.0306	0.0070	0.0068	0.0067	0.0065
Methyl ethyl mercaptan	0.0080	0.0082	0.0106	0.0091	0.0072	0.0079	0.0074	0.0073
Dimethyl disulfide	0.0071	0.0074	0.0085	0.0075	0.0070	0.0068	0.0067	0.0065

Source: DMS Hydrogen Laboratory

Table 12: Sulfur Compound MDL Calculation Results

	Ret. Time (Minutes)	MDL-PPM	Std. Dev.	t-test VALUE
Hydrogen sulfide	9.908	0.0042	0.00141	2.998
Carbonyl sulfide	11.133	0.0040	0.00126	3.143
Methyl mercaptan	22.046	0.0016	0.00054	2.998
Ethyl mercaptan	30.102	0.0027	0.00091	2.998
Carbon disulfide	31.670	0.0025	0.00082	2.998
Dimethyl sulfide	32.249	0.0071	0.00238	2.998
Methyl ethyl mercaptan	39.271	0.0035	0.00115	2.998
Dimethyl disulfide	48.173	0.0019	0.00063	2.998

Source: DMS Hydrogen Laboratory

Oxygen

Although the ECD has adequate sensitivity for this analysis, a satisfactory calibration could not be obtained because of inconsistent detector response between successive injections. A replacement ECD exhibited similar behavior. The cause of this unstable response has not been determined. Future work will be required to determine whether an ECD method for the analysis of oxygen in hydrogen fuel can be developed.

The sensitivity of the PDHID for oxygen is not sufficient to achieve the MDL required by the specification in *SAE J2719*. Mass spectrometry is one possible alternative analytical approach for oxygen analysis. Recently, a CRDS module for oxygen has been introduced. In view of the successful application of CRDS to the determination of water and ammonia, this is another potential alternative method for the determination of oxygen in hydrogen.

System 2: Determination of Helium, Argon, Oxygen, Nitrogen, Carbon Dioxide, THCs, and Methane

Helium by GC-TCD

Figure 8 shows a representative TCD chromatogram for helium. Table 13 lists the helium concentrations used for the initial calibration. The TCD calibration report for He is shown in Figure 9. A correlation coefficient of 0.992 was obtained for the He calibration.

Table 13: Helium Calibration Standards

Level	Standard ID	Conc. (ppm)
Level 1	SHS-143	48.5
Level 2	SHS-144	193
Level 3	SHS-145	301
Level 4	SHS-146	400
Level 5	SHS-147	608

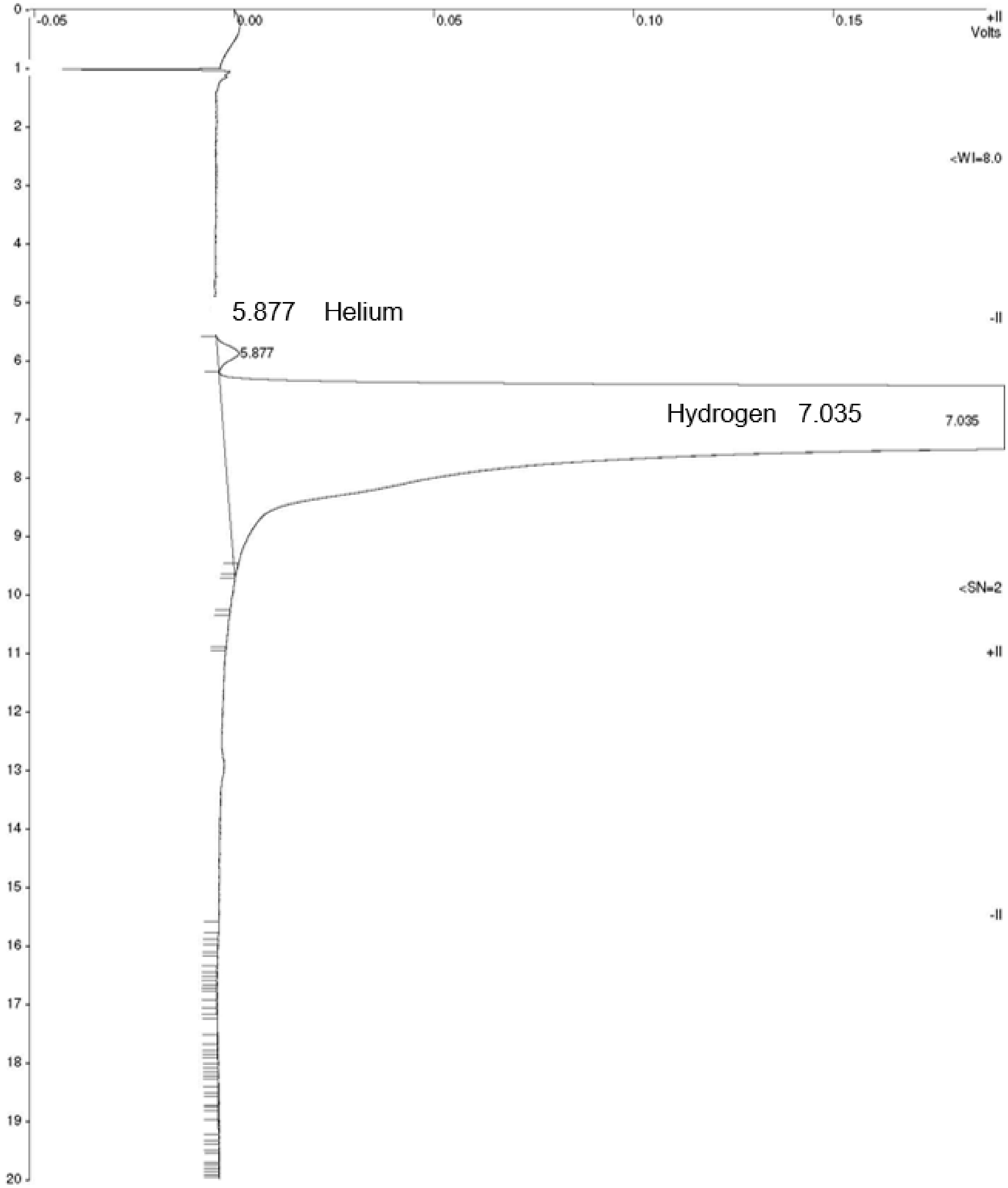
Source: DMS Hydrogen Laboratory

CO, CO_2, Methane, and THC by GC-FID

Figure 10 shows an FID chromatogram for CO, CO_2, Methane, and THC. The upsets in the baseline during the first three minutes of the run are due to changes in the GC column pressure that occur as the valves in the sampling system are switched. The elution time for carbon monoxide is approximately 8.15 minutes. However, as the chromatogram shows, the FID detector signal is too weak to identify carbon monoxide at the levels required.

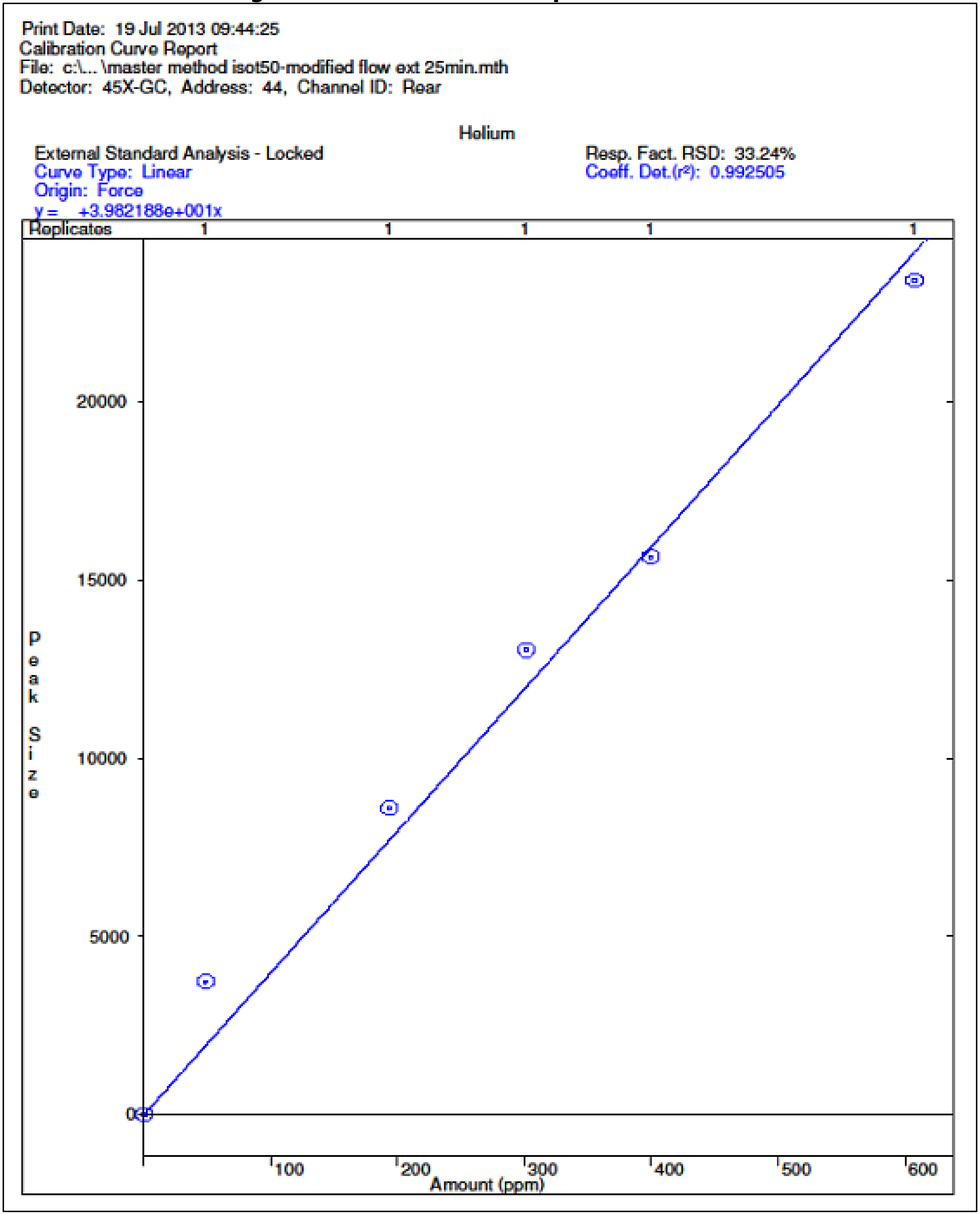
Table 14 lists the concentrations used for the initial FID calibration. Propane was used in the calibration mixtures as a surrogate non-methane hydrocarbon. The THC concentration at each level is the sum of the methane and propane concentrations.

Figure 8: System 2 TCD Chromatogram for Helium



Source: DMS Hydrogen Laboratory

Figure 9: TCD Calibration Report for Helium



Print Date: 19 Jul 2013 09:44:25
Calibration Curve Report
File: c:\...\master method isot50-modified flow ext 25min.mth
Detector: 45X-GC, Address: 44, Channel ID: Rear

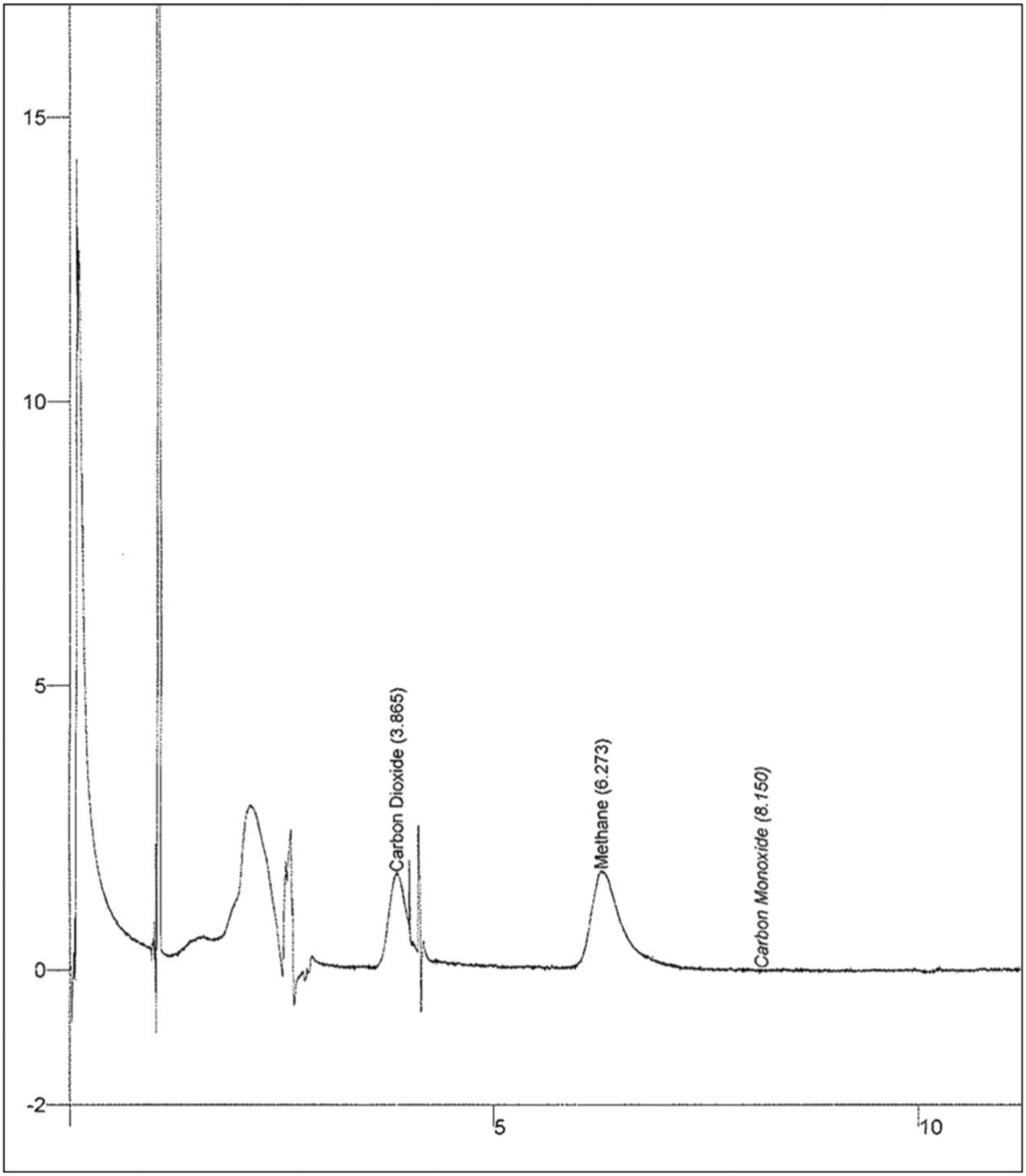
Helium

External Standard Analysis - Locked
Curve Type: Linear
Origin: Force
y = +3.982188e+001x

Resp. Fact. RSD: 33.24%
Coeff. Det.(r^2): 0.992505

Source: DMS Hydrogen Laboratory

Figure 10: System 2 FID Chromatogram



Source: DMS Hydrogen Laboratory

Table 14: Calibration Mixture Concentrations for System 2 FID

Level	Standard ID	Methane	Propane	THC	CO_2	CO
Level 1	SHS-159	0.5 ppm	0.5 ppm	2.0 ppm	0.5 ppm	.05 ppm
Level 2	SHS-158	1.0 ppm	1.0 ppm	4.0 ppm	1.0 ppm	0.1 ppm
Level 3	SHS-157	2.0 ppm	2.0 ppm	8.0 ppm	2.0 ppm	0.2 ppm
Level 4	SHS-156	3.0 ppm	3.0 ppm	12.0 ppm	3.0 ppm	0.3 ppm
Level 5	SHS-155	5.0 ppm	5.0 ppm	20.0 ppm	5.0 ppm	0.5 ppm

Source: DMS Hydrogen Laboratory

The FID calibration reports for THC, CH_4, and CO_2 are shown in Figures 11-13. As the graphs show, highly precise and stable calibrations were obtained, with correlation coefficients greater than 0.99 for all three analytes.

GC-PDHID: Nitrogen and Argon

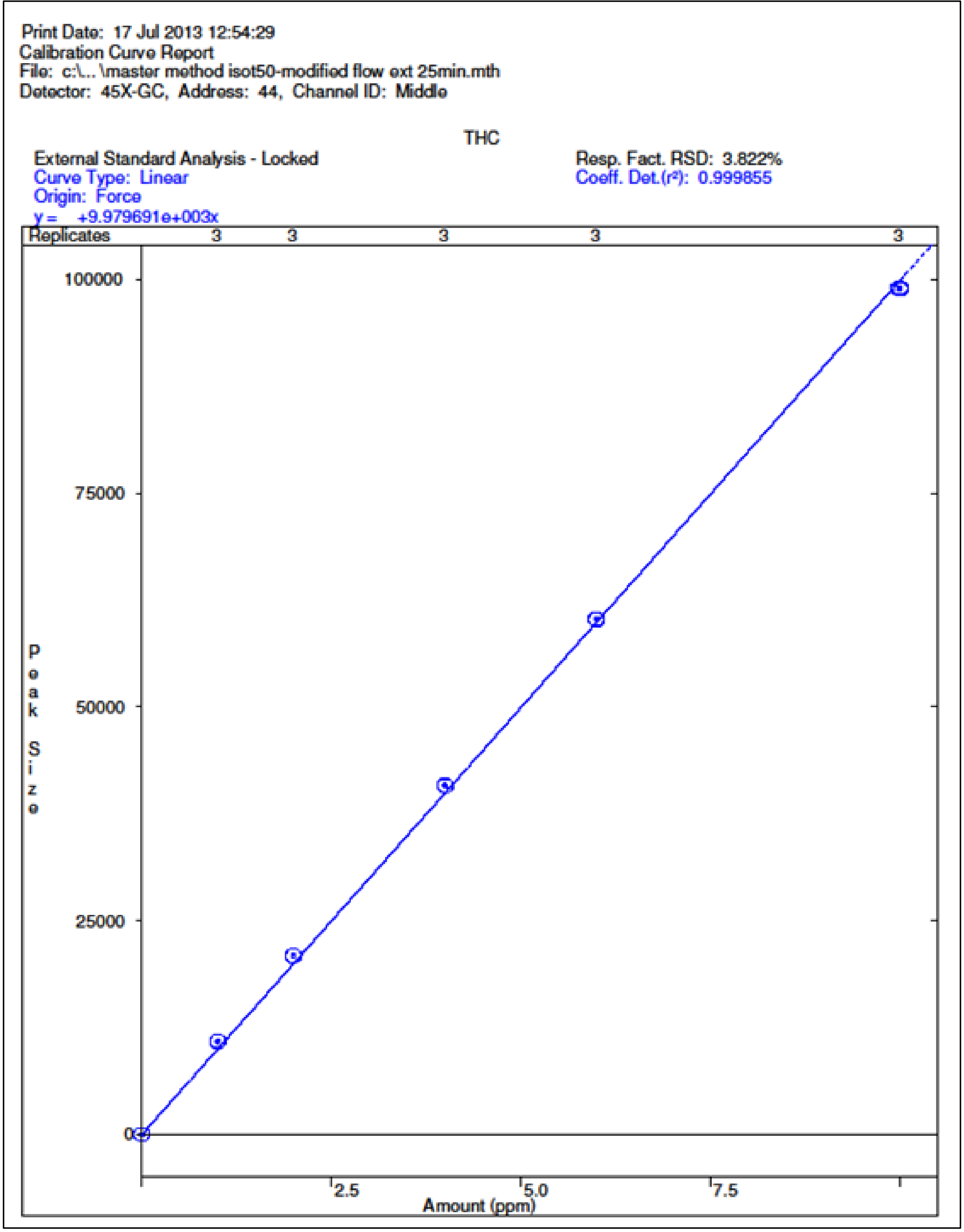
Figure 14 shows a PDHID chromatogram for nitrogen, argon, and oxygen. Table 15 lists the concentrations used for the initial PDHID calibration. The calibration reports for nitrogen and argon are shown in Figures 14-15. The PDHID sensitivity for oxygen is too low to reach the detection limit required by *SAE J2719*.

Table 15: Calibration Mixture Concentrations for System 2 PDHID

Calibration Level	Standard ID	Nitrogen	Argon	O_2	Argon+O_2
Level 1	SHS-190	25	25	1	26
Level 2	SHS-189	50	50	2	52
Level 3	SHS-194	97	97	5	102
Level 4	SHS-192	200	200	10	210
Level 5	SHS-193	398	418	20	418

Source: DMS Hydrogen Laboratory

Figure 11: FID Calibration Report for THCs



Print Date: 17 Jul 2013 12:54:29
Calibration Curve Report
File: c:\...\master method isot50-modified flow ext 25min.mth
Detector: 45X-GC, Address: 44, Channel ID: Middle

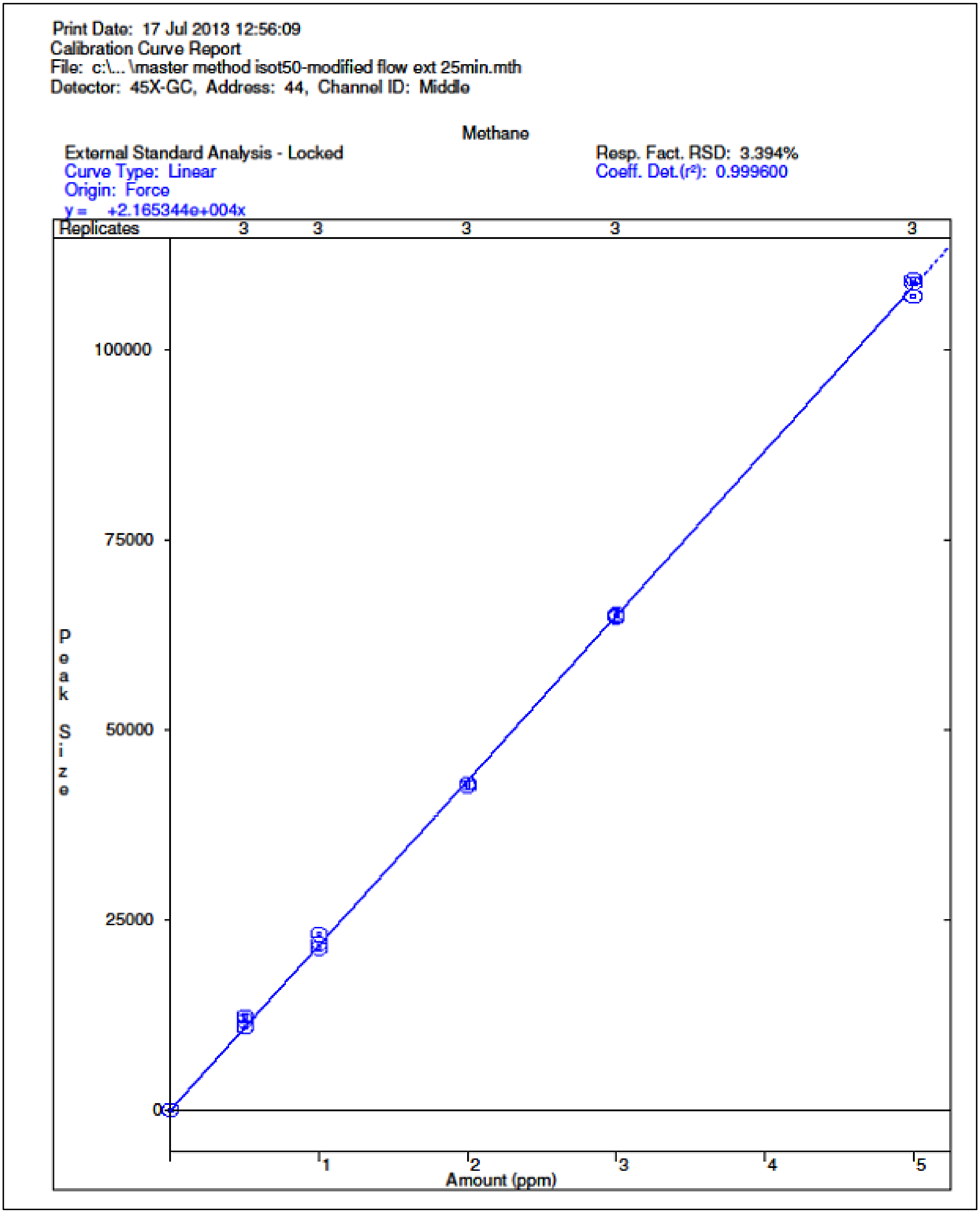
THC

External Standard Analysis - Locked
Curve Type: Linear
Origin: Force
y = +9.979691e+003x

Resp. Fact. RSD: 3.822%
Coeff. Det.(r^2): 0.999855

Source: DMS Hydrogen Laboratory

Figure 12: FID Calibration Report for Methane



Print Date: 17 Jul 2013 12:56:09
Calibration Curve Report
File: c:\...\master method isot50-modified flow ext 25min.mth
Detector: 45X-GC, Address: 44, Channel ID: Middle

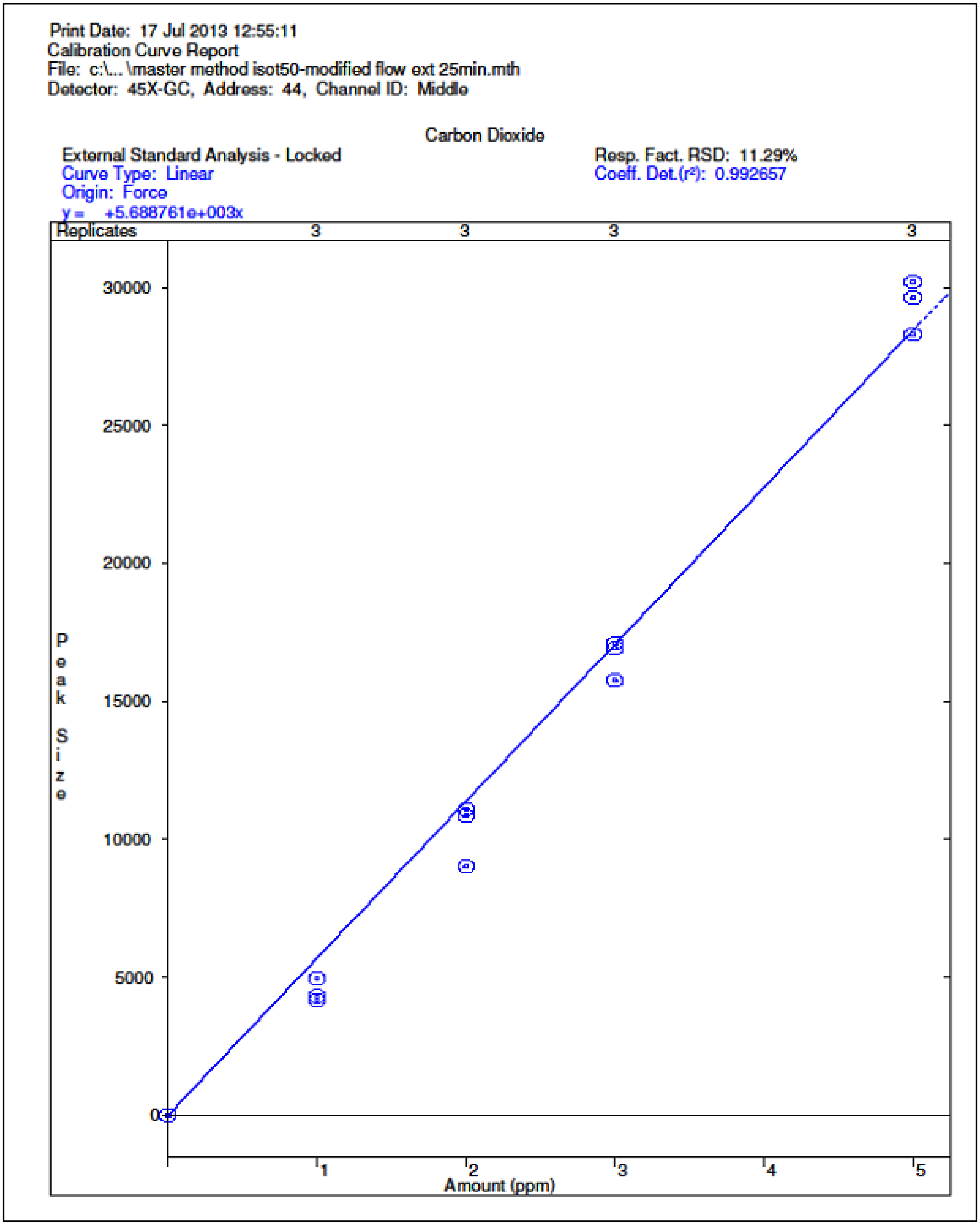
Methane

External Standard Analysis - Locked
Curve Type: Linear
Origin: Force
y = +2.165344e+004x

Resp. Fact. RSD: 3.394%
Coeff. Det.(r^2): 0.999600

Source: DMS Hydrogen Laboratory

Figure 13: FID Calibration Report for Carbon Dioxide



Print Date: 17 Jul 2013 12:55:11
Calibration Curve Report
File: c:\...\master method isot50-modified flow ext 25min.mth
Detector: 45X-GC, Address: 44, Channel ID: Middle

Carbon Dioxide

External Standard Analysis - Locked
Curve Type: Linear
Origin: Force
y = +5.688761e+003x

Resp. Fact. RSD: 11.29%
Coeff. Det.(r^2): 0.992657

Source: DMS Hydrogen Laboratory

With the analytical columns used, Ar and O_2 co-elute. However, the PDHID sensitivity for O_2 is much lower than for Ar, so that there is not a significant interference from the oxygen in the calibration standard mixtures. N_2 can be reliably identified and quantified at the required levels using the PDHID. Helium can be reliably identified and quantified at the required levels utilizing TCD. THC, Methane, and CO_2 can be reliably identified and quantified at the required levels utilizing FID. Carbon monoxide is not detectable at the required levels under the GC-FID conditions utilized in the laboratory studies. Method detection limits were determined in accordance with procedures outlined in U.S. EPA 40 CFR Section 136 Appendix D. The calculated method detection limits for the System 2 analytes are shown in Table 16. Table 17 lists the *SAE J2719* specifications along with these MDLs.

Table 16: System 2 MDL Calculations

Calc. Conc. (ppm)	19.87	19.87	0.41	0.41	0.41	29.80
	PDHID	PDHID	FID	FID	FID	TCD
MDL	Argon	Nitrogen	THC	CO2	Methane	Helium
1	27.59	72.41	0.17	0.75	0.37	44.67
2	27.62	72.37	0.18	0.8	0.41	43.49
3	27.83	72.17	0.18	0.87	0.43	36.42
4	27.39	72.61	0.18	0.89	0.41	42.50
5	27.51	72.49	0.18	0.99	0.37	36.16
6	27.69	72.31	0.18	0.92	0.40	36.36
7	27.47	72.53	0.18	0.98	0.34	36.37
8	28.01	71.99	0.18	0.87	0.42	34.63
9	27.6	72.4	0.18	0.86	0.45	34.3
Mean	27.63	72.36	0.18	0.88	0.40	38.32
ST DEV	3.826	3.826	0.004	0.081	0.035	6.990
MDL	11.08	11.08	0.012	0.23	0.10	20.25

Source: DMS Hydrogen Laboratory

The PDHID calibration reports for nitrogen and argon are shown in Figures 14 and 15. Correlation coefficients of 0.952 for nitrogen and 0.990 for argon were obtained. As noted above, the PDHID sensitivity for oxygen was too low to meet the *SAE J2719* specification.

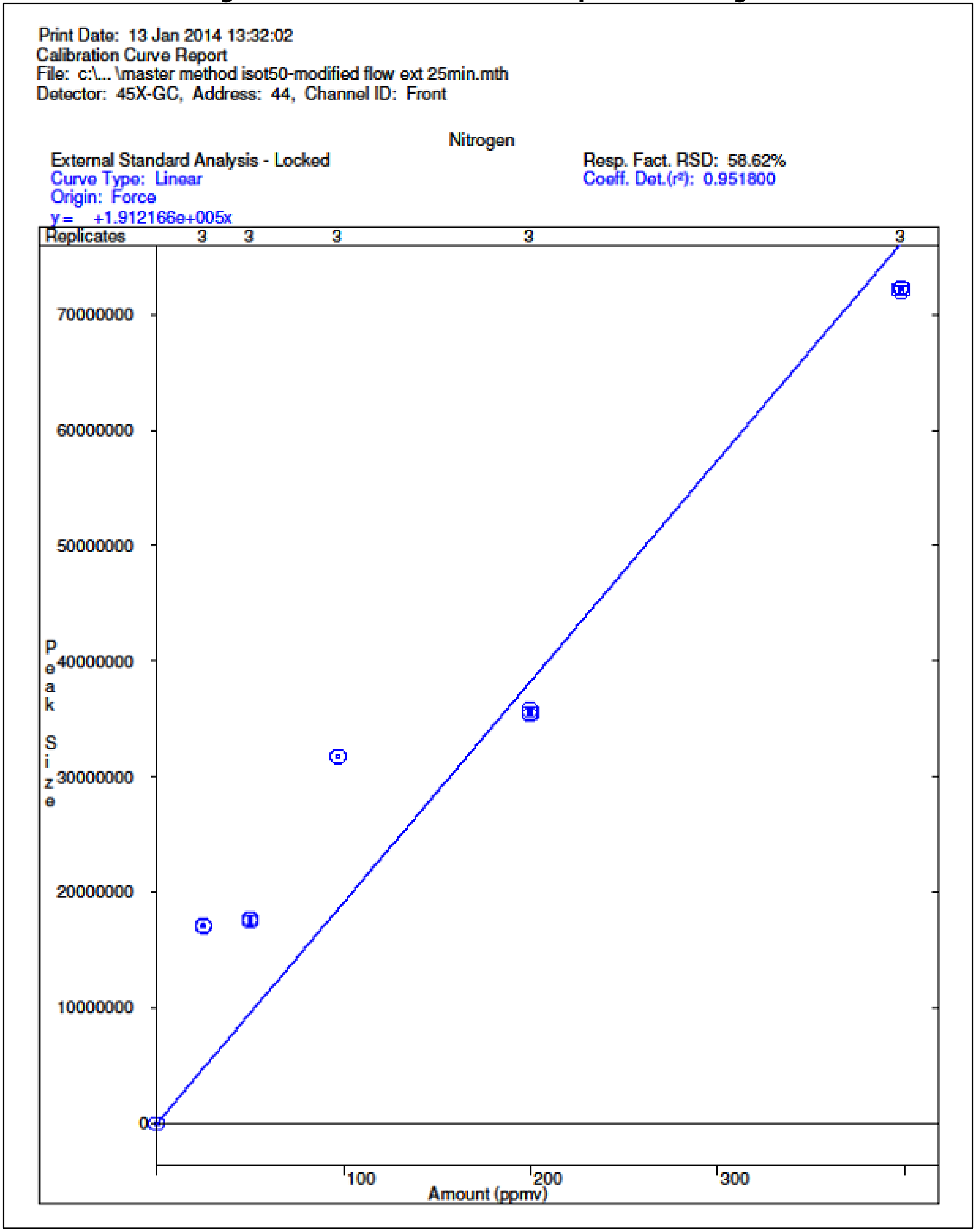


Figure 14: PDHID Calibration Report for Nitrogen

Print Date: 13 Jan 2014 13:32:02
Calibration Curve Report
File: c:\... \master method isot50-modified flow ext 25min.mth
Detector: 45X-GC, Address: 44, Channel ID: Front

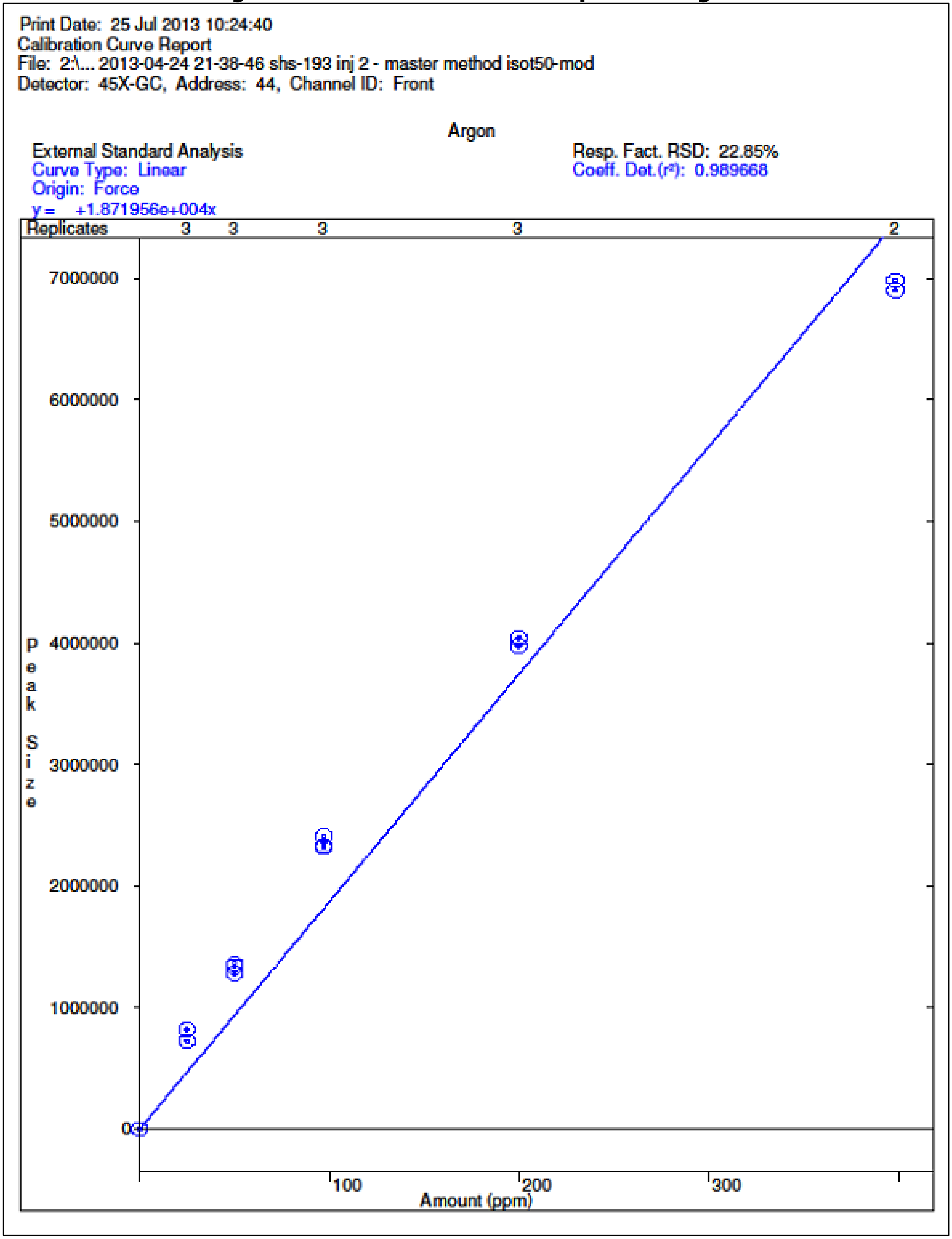
Nitrogen

External Standard Analysis - Locked
Curve Type: Linear
Origin: Force
y = +1.912166e+005x

Resp. Fact. RSD: 58.62%
Coeff. Det.(r²): 0.951800

Source: DMS Hydrogen Laboratory

Figure 15: PDHID Calibration Report for Argon



Print Date: 25 Jul 2013 10:24:40
Calibration Curve Report
File: 2:\... 2013-04-24 21-38-46 shs-193 inj 2 - master method isot50-mod
Detector: 45X-GC, Address: 44, Channel ID: Front

Argon

External Standard Analysis
Curve Type: Linear
Origin: Force
$y = +1.871956e+004x$

Resp. Fact. RSD: 22.85%
Coeff. Det.(r^2): 0.989668

Source: DMS Hydrogen Laboratory

Table 17: System 2 MDLs and *SAE J2719* Reporting Limits

Analyte	Detector	MDL	*SAE J2719* limits
Ar	PDHID	11.08 ppm	100 ppm
N_2	PDHID	11.08 ppm	100 ppm
CH_4	FID	0.044 ppm	2 ppm
CO_2	FID	0.234 ppm	2 ppm
THC	FID	0.012 ppm	2 ppm
He	TCD	20.24 ppm	300 ppm
CO*		above RL	2 ppm
O_2**		above RL	5 ppm

* CO could not be detected at the *SAE J2719* RL.

** O_2 could not be resolved from Ar.

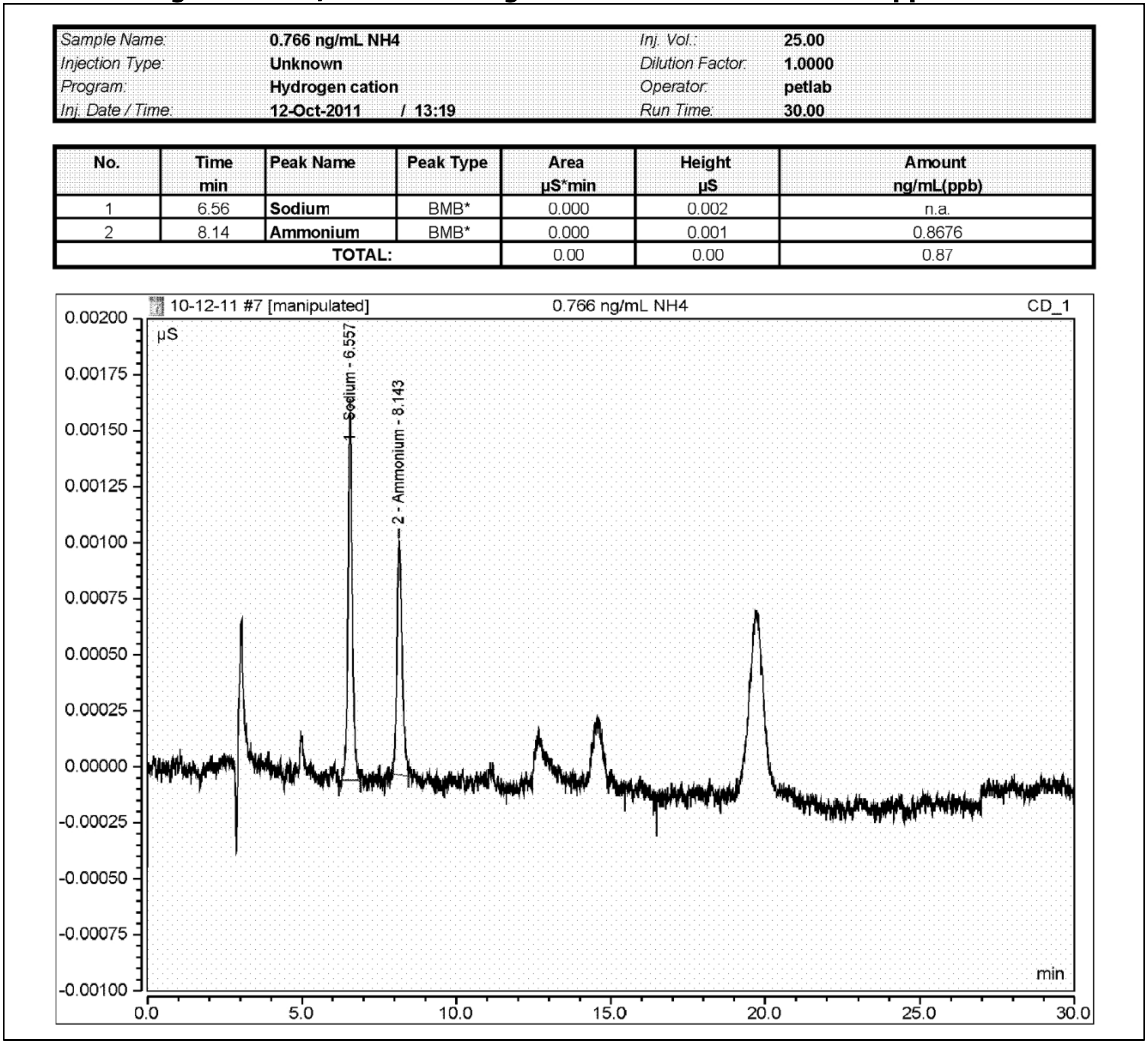
Source: DMS Hydrogen Laboratory

IC: Evaluation for NH_3

ASTM method *D7550-09* was developed for the determination of cations in fuel cell feed gases using ion chromatography with a conductivity detector (IC/CD). This method was validated over a concentration range of 0.1 to 2.0 ppm ammonium ion. However, when *SAE J2719* was issued two years later, in September 2011, the maximum allowable concentration for ammonia in hydrogen fuel was set at 0.1 ppm, the bottom of the calibration range. An effort was made to extend the calibration range by modifying the procedure outlined in *D7550-09*. A lower calibration limit of at least 0.02 ppm is needed for the determination of ammonia at 0.1 ppm with sufficient precision for future regulatory enforcement. Standards were prepared to test the sensitivity of the IC/CD system at the level required. Figure 16 shows an ion chromatogram of a mixture of cations at 0.1 ppb.

Samples of hydrogen gas containing ammonia were connected to a sparger tube assembly with the fritted glass diffusion tip submersed in a dilute sulfuric acid solution (10.0 ml of 0.01N H_2SO_4). The gas was bubbled into the acid sample at a rate of ~ 50ml/min as indicated on a calibrated flow meter corrected for hydrogen. After a timed interval of sparging (gas diffusion into liquid), the gas sparger tube was removed and samples of the acid trapping solution were analyzed by IC/DC on a Dionex 5000. Known concentrations of ammonia in hydrogen were used as samples and the IC results were contrasted with the known concentrations. Experimental results were less than optimal for an analytical determination of ammonia. The calculated trapping efficiency (IC concentration / known concentration x 100 percent) varied from sample to sample. Initial samples of highly concentrated ammonia (400 ppmv) in hydrogen demonstrated a trapping efficiency of ~ 85 percent. Samples of hydrogen with 50 ppmv ammonia demonstrated ~ 78 percent efficiency. Samples at low levels—but still double the SAE *J-2719* reporting limit of 0.200 ppmv ammonia in hydrogen—resulted in no detectable ammonium ion in the trapping solution.

Figure 16: IC/CD Chromatogram of Cation Mixture at 0.1 ppb



Sample Name:	**0.766 ng/mL NH4**	Inj. Vol.:	**25.00**
Injection Type:	**Unknown**	Dilution Factor:	**1.0000**
Program:	**Hydrogen cation**	Operator:	**petlab**
Inj. Date / Time:	**12-Oct-2011 / 13:19**	Run Time:	**30.00**

No.	Time min	Peak Name	Peak Type	Area µS*min	Height µS	Amount ng/mL(ppb)
1	6.56	**Sodium**	BMB*	0.000	0.002	n.a.
2	8.14	**Ammonium**	BMB*	0.000	0.001	0.8676
		TOTAL:		0.00	0.00	0.87

Source: DMS Hydrogen Laboratory

In another test, 10.0 ml of acid solution were charged into a clean (sampled and tested by IC to contain no residual ammonium ion) trapping bottle. The gas sparging apparatus was connected to the gas cylinder containing reference standard SHS-52 with 0.4 ppmv ammonia in hydrogen. The sample was sparged into the trapping solution at a rate of 46.7 ml/min for 3.0 minutes representing 140.1 ml of total gas volume sparged into acid trap. The acid trap solution was then analyzed by IC. The resulting ion chromatogram indicated no detectable level of ammonia present.

If the trapping were 100 percent efficient, this sample would be equivalent to 4.5 ppb of ammonia in hydrogen, as shown in the sample calculation below:

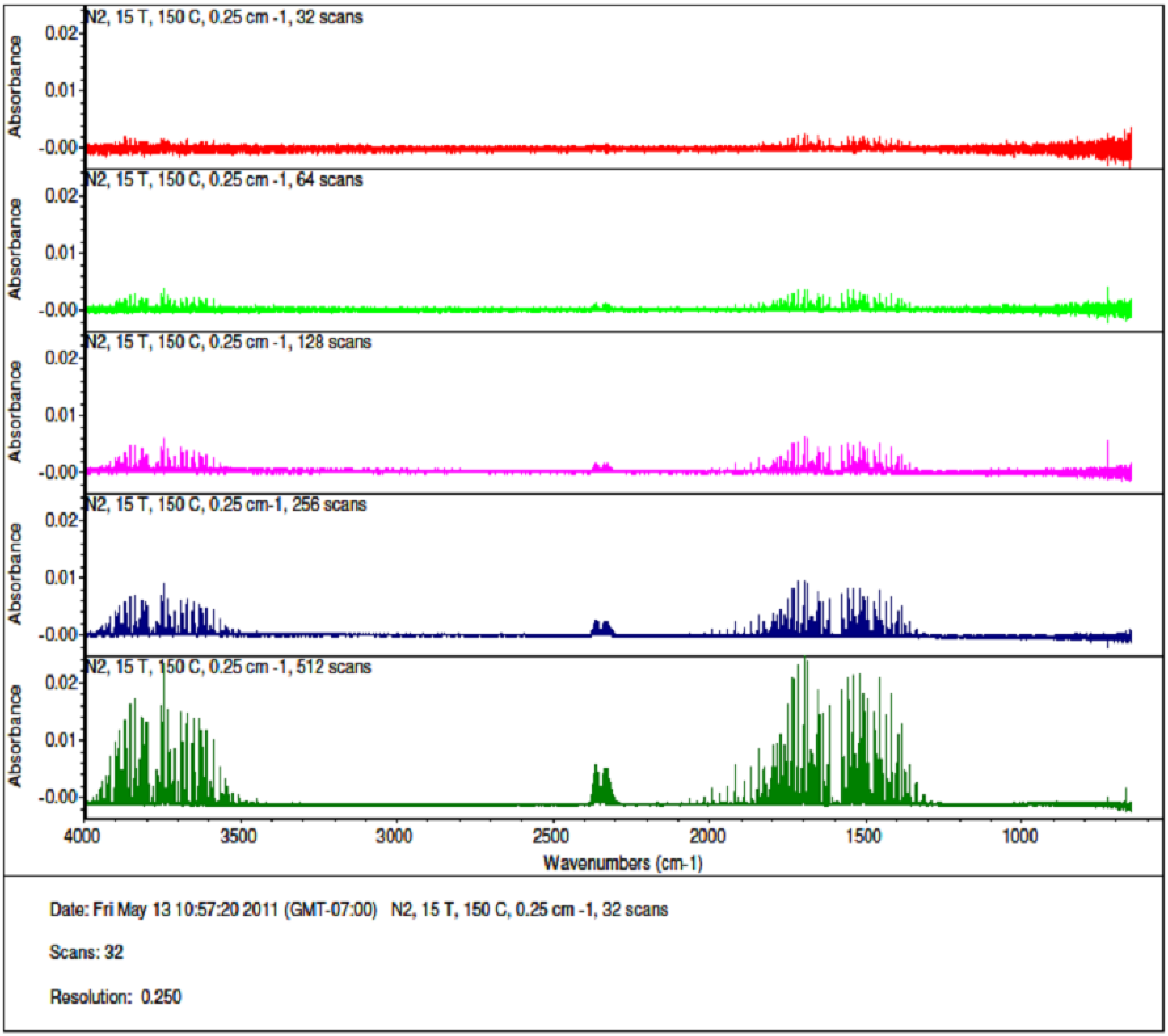
$$140.1\,ml.Gas \times \frac{0.400x10^{-6}mlNH_3}{ml.Gas}\ x\ \frac{1moleNH_3gas}{22.4x10^3mlNH^3}\,x\,\frac{1moleNH_4{}^+}{1molNH_3}\,x\,\frac{18.0gNH_4{}^+}{molNH_4{}^+}\,x\,\frac{1}{10.0ml}=\frac{4.50x10^{-9}}{ml}=4.5\,ppb$$

Standard ionic solutions containing ammonium have been prepared down to 0.76 ppb of ammonia. Ammonia in solution is both identifiable and quantifiable by IC using the current system method. However, there does not appear to be any way to quantitatively transfer ammonia entrained in a gaseous sample to the IC eluant. Therefore, IC cannot be applied to the analysis of hydrogen fuel. Since the IC investigation of ammonia failed, the determination of formaldehyde by IC was not pursued.

FTIR: Determination of CO, CO_2, NH_3, H_2O, and Hydrocarbons

The FTIR was evaluated for the identification and quantification of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and related hydrocarbons, ammonia (NH_3), and water vapor (H_2O). Each indicated impurity or analyte has a distinguishable infrared spectrum that differentiates it from other compounds. The amount of infrared absorption is directly proportional to the concentration each analyte. EPA Method 320 gives general guidance on analytical protocols and data interpretation, but specific information regarding instrumental settings depends upon the matrix being tested. A series of experiments was undertaken to determine the optimal parameters for hydrogen fuel analysis. Figure 17 shows the background absorption in the cell was recorded at a fixed resolution of 0.25 cm^{-1} averaged over a number of scans ranging from 32 to 512. The peaks are due to water vapor and CO_2. Figure 18 shows a region with no background absorption so that the differences in baseline noise may be seen more clearly. The plots in Figure 17 are all on the same scale, so it is apparent that increasing the number of scans decreases the baseline noise. Lower baseline noise increases sensitivity, so that analytes can be detected at lower levels; however, increasing the number of scans from 32 to 512 has increases the analysis time from 1:36 to 25:47 minutes.

Figure 17: Background Infrared Absorption of the Cell with Increasing Number of Scans



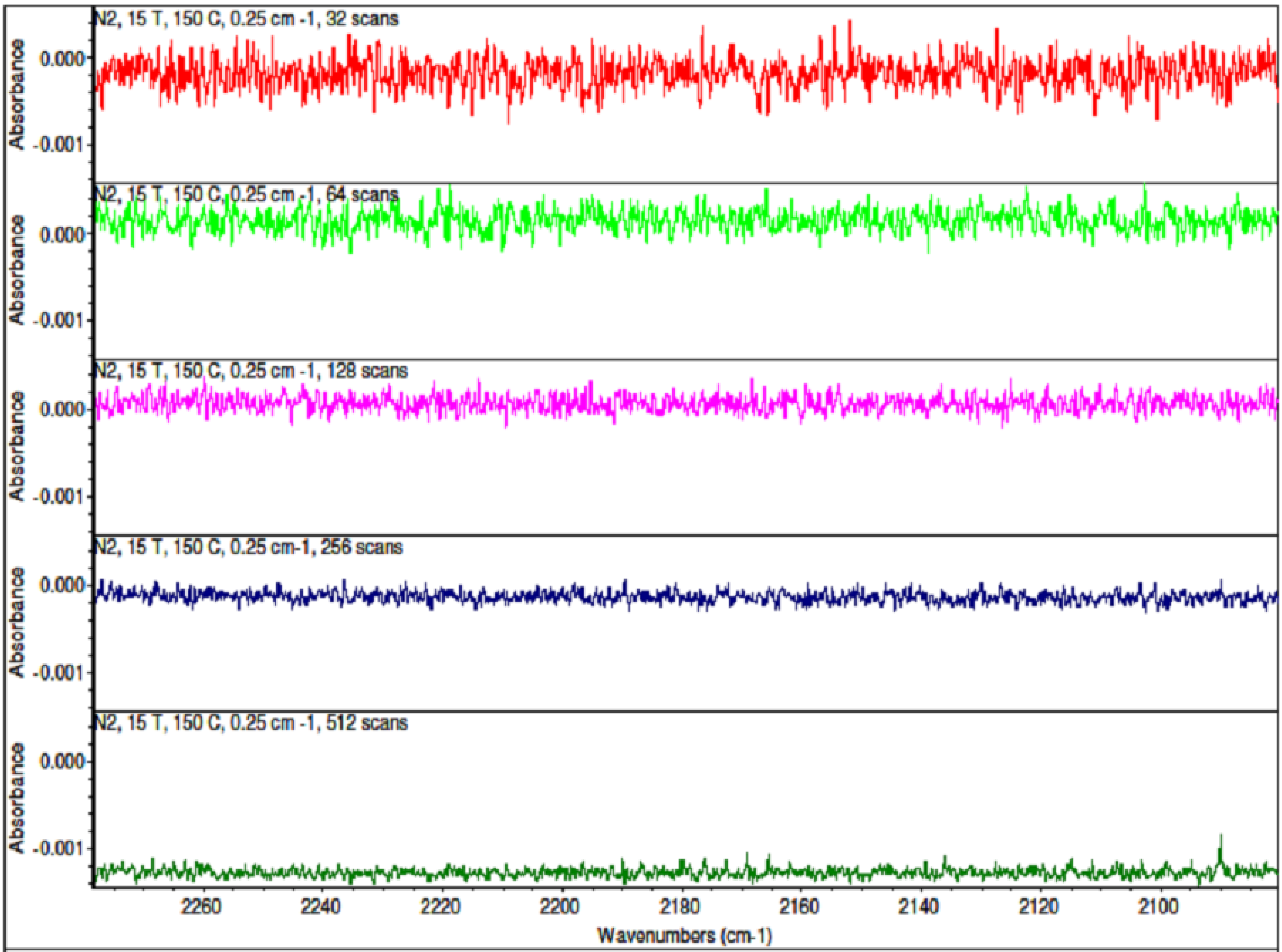
Date: Fri May 13 10:57:20 2011 (GMT-07:00) N2, 15 T, 150 C, 0.25 cm -1, 32 scans

Scans: 32

Resolution: 0.250

Source: DMS Hydrogen Laboratory

Figure 18: Baseline Noise as a Function of Scan Number



Date: Fri May 13 10:57:20 2011 (GMT-07:00) N2, 15 T, 150 C, 0.25 cm -1, 32 scans

Scans: 32

Resolution: 0.250

Source: DMS Hydrogen Laboratory

Table 18 shows the Peak-Peak, Root Means Square noise, maximum CO_2 absorbance, signal-to-noise ratio, and analysis time as a function of the number of scans collected from the data above:

Table 18: Analysis Parameters as a Function of Number of Scans

Number of Scans	Peak-Peak noise	Root Means Square noise	Maximum CO_2 Absorbance	S/N	Analysis Time (min)
32 Scans	0.001395	0.0002081	0.0021	10.1	1:36
64 Scans	0.001123	0.0001527	0.0033	21.6	3:13
128 Scans	0.0007577	0.0001091	0.0060	55.0	6:26
256 Scans	0.0005583	0.00007469	0.0090	120.5	12:53
512 Scans	0.0003893	0.00005354	0.024	444.4	25:47

Source: DMS Hydrogen Laboratory

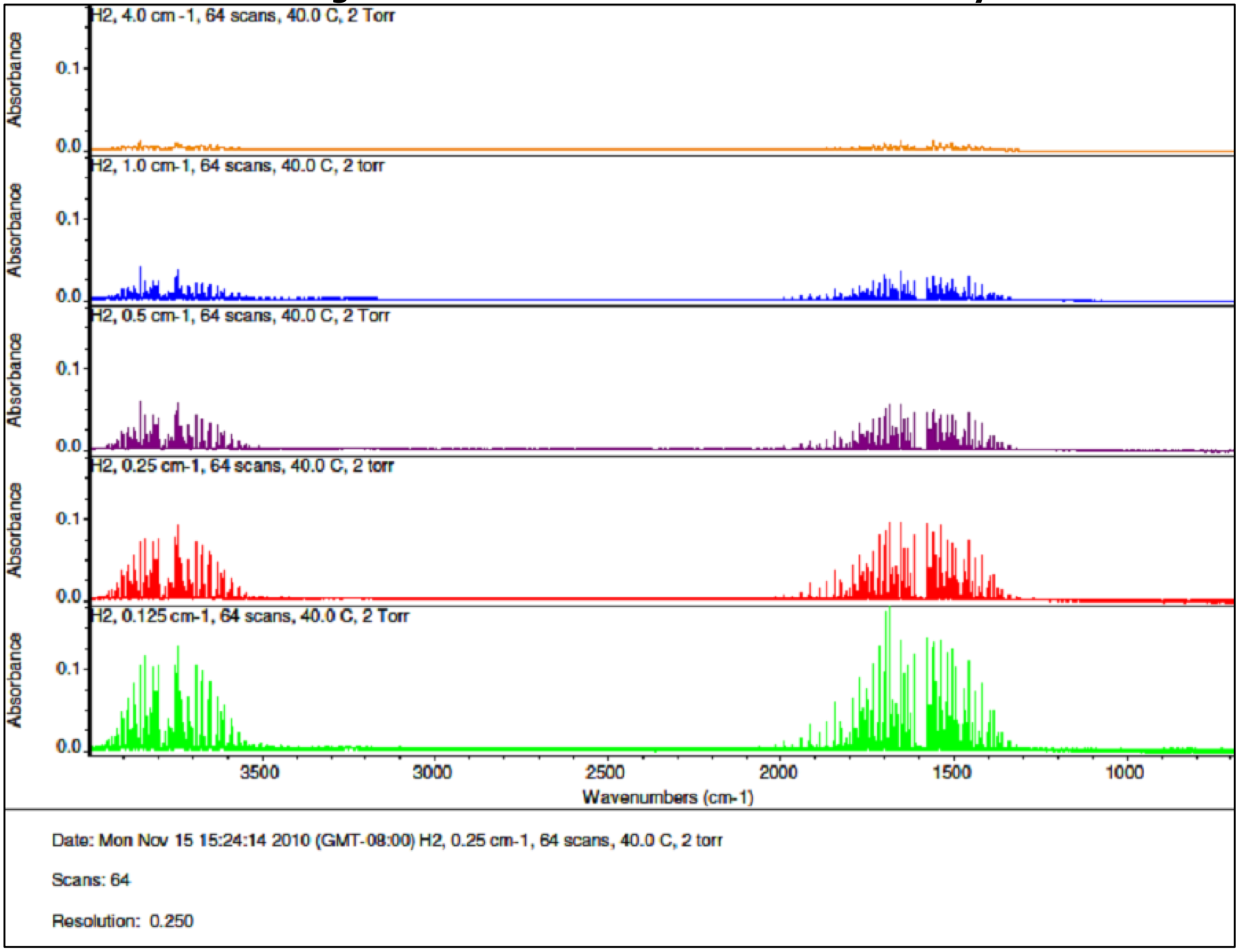
Another series of experiments was undertaken to determine the optimal parameters for sample analysis. A hydrogen-filled cell was analyzed with a fixed number of scans and various resolution settings on the spectrometer as shown in Figure 19. All spectra are plotted on a common scale, so it is clear that increasing the resolution from 4 cm^{-1} to 0.125 cm^{-1} gives a dramatic increase to sensitivity. Increasing the resolution also increases the collection time for an analysis, from 0:39 at 4 cm^{-1} to 6:06 for 0.125 cm^{-1}, as shown in Table 19.

Table 19: Sensitivity and Analysis Time vs. Resolution

Resolution (cm^{-1})	Maximum Absorbance (AU)	Analysis Time (min)
4.0	0.010	0:39
1.0	0.040	1:44
0.5	0.057	1:46
0.25	0.093	3:13
0.125	0.17	6:06

Source: DMS Hydrogen Laboratory

Figure 19: Effect of Resolution on Sensitivity



Date: Mon Nov 15 15:24:14 2010 (GMT-08:00) H2, 0.25 cm-1, 64 scans, 40.0 C, 2 torr

Scans: 64

Resolution: 0.250

Source: DMS Hydrogen Laboratory

In order to achieve the goals of a rapid analysis with sufficient sensitivity, a maximum target analysis time of ~ 6 min time was chosen. To decrease the baseline noise without extending the analysis time, the number of scans was increased while the resolution was reduced. The optimized parameters selected for data collection are 128 scans at 0.25 cm-1 resolution, for an analysis time of 6:26 minutes. These instrument settings were used throughout this project.

A set of ten calibration mixtures of the FTIR analytes in hydrogen were prepared with the concentrations shown in Table 20. Figure 20 shows the observed FTIR spectrum of calibration mixture 5, which corresponds roughly to the maximum allowed concentrations set by *SAE J2719*. Data was collected well below the required reporting limits to determine the limits of detection. The calibration reports generated by the instrument are shown in Figures 21 – 25.

Correlation coefficients for all analytes were ≥ 0.995. This meets the initial calibration acceptance criteria of EPA Method 8000C. The two lowest concentrations of carbon monoxide and the five lowest concentrations for ammonia were below the limit of detection with the data collection parameters that had been selected. Accordingly, the calibrations for carbon monoxide and ammonia were based on only eight and five data points, respectively. The lowest concentration for the carbon monoxide calibration was approximately 0.25 times the *SAE J2719* limit and the lowest concentration for ammonia was 3 times the *SAE J2719* limit.

Based on the results of this calibration, it was concluded that analysis of ammonia by FTIR could not achieve sufficient sensitivity.

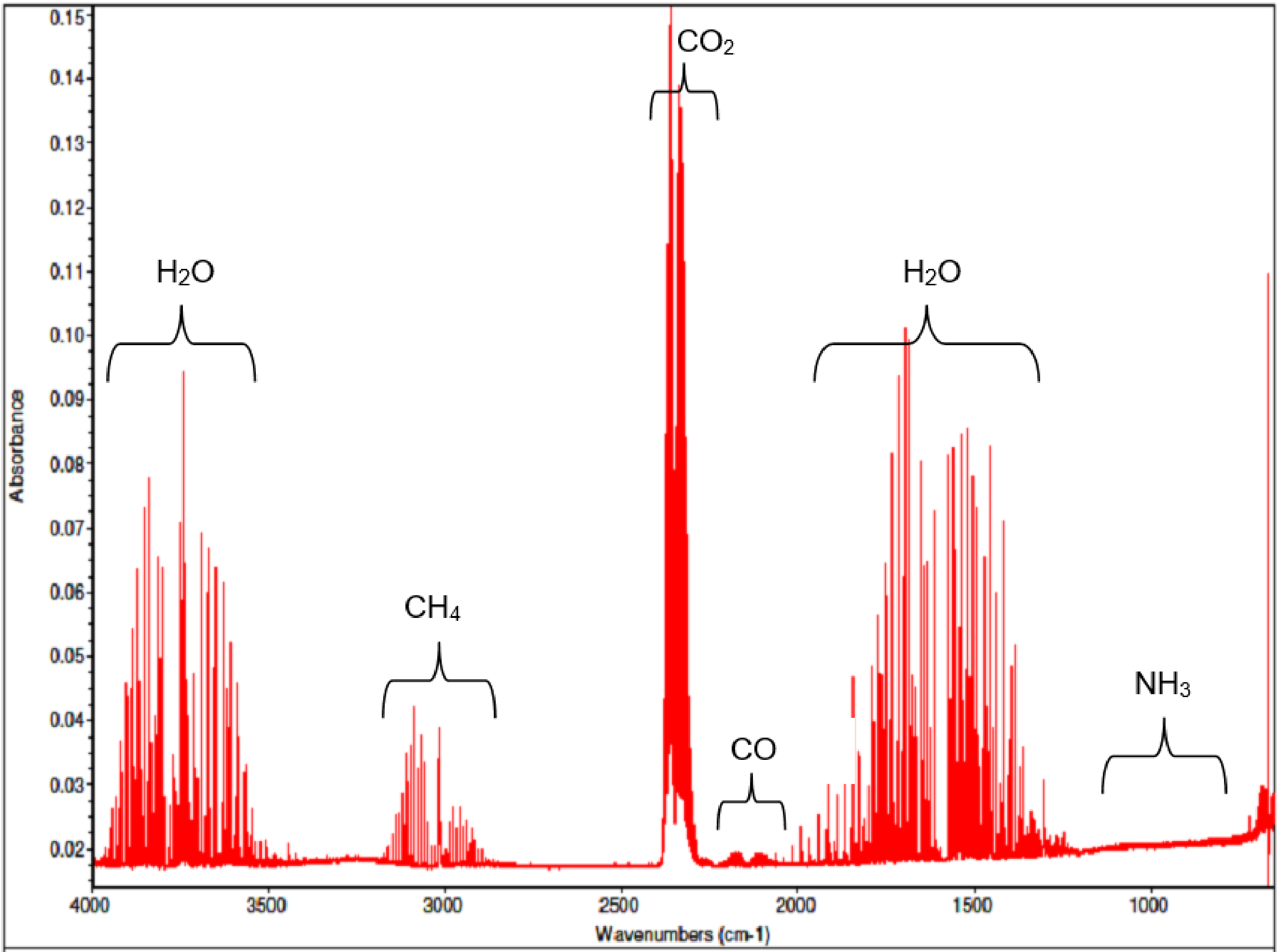
In addition, a definite high bias can be seen in the water calibration, 20 times higher than for any other analyte. This bias indicates that the water calibration is not valid. The problem was later found to be the result of a cylinder of reference hydrogen contaminated with water. Trace moisture in commercial hydrogen cylinders can interfere with the determination of several analytes in hydrogen fuel, including ammonia and formaldehyde. Although cylinder hydrogen can be dried before use, this is inconvenient and expensive as the primary means of insuring a water-free reference hydrogen gas. A reliable source of truly dry reference hydrogen with less than 500 ppb is required for fuel quality analysis by FTIR. There was not sufficient time to repeat the FTIR water analysis after this problem was resolved. It is possible that FITR would be an acceptable method for water determination in hydrogen fuel.

Table 20: Calibration Mixture Concentrations for FTIR
(concentrations in ppm)

Calib. Level	**CO**	**CO_2**	**Methane**	**Ammonia**	**Water**
Level 1	-100	0.122	0.122	-100	0.307
Level 2	-100	0.201	0.201	-100	0.505
Level 3	0.052	0.522	0.522	-100	1.31
Level 4	0.1	0.999	0.999	-100	2.51
Level 5	0.199	1.991	1.991	-100	4.998
Level 6	0.295	2.953	2.953	0.295	7.414
Level 7	0.406	4.06	4.06	0.406	10.196
Level 8	0.514	5.142	5.142	0.514	12.912
Level 9	0.729	7.287	7.287	0.729	18.297
Level 10	0.902	9.016	9.016	0.902	22.639

Source: DMS Hydrogen Laboratory

Figure 20: FTIR Spectrum of Fixed Gas Calibration Mixture at the Maximum Concentrations Allowed



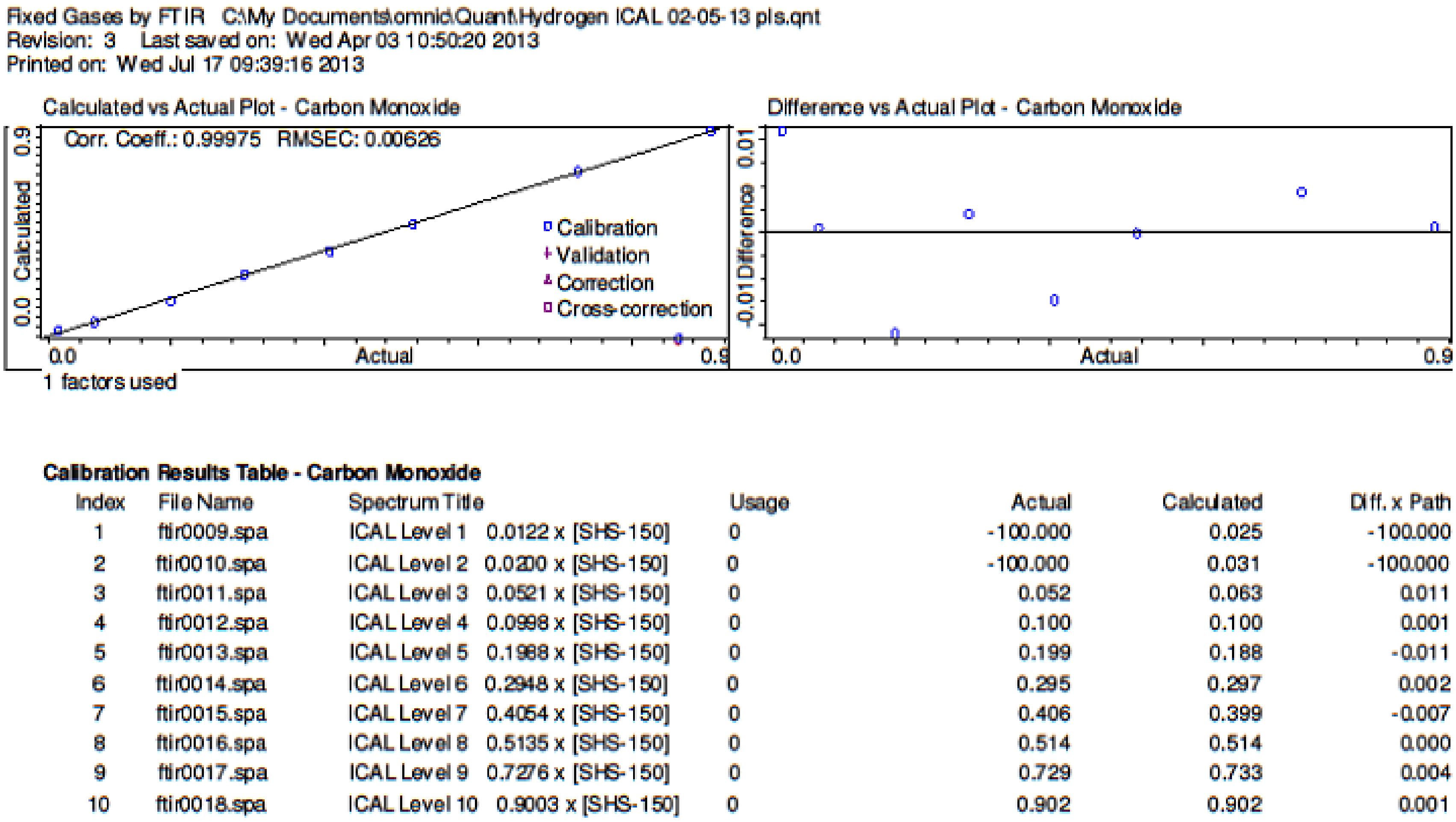
Date: Tue Feb 05 11:43:03 2013 (GMT-08:00) ICAL Level 5 0.1988 x [SHS-150]

Scans: 128

Resolution: 0.250

Source: DMS Hydrogen Laboratory

Figure 21: FTIR Calibration Report for Carbon Monoxide



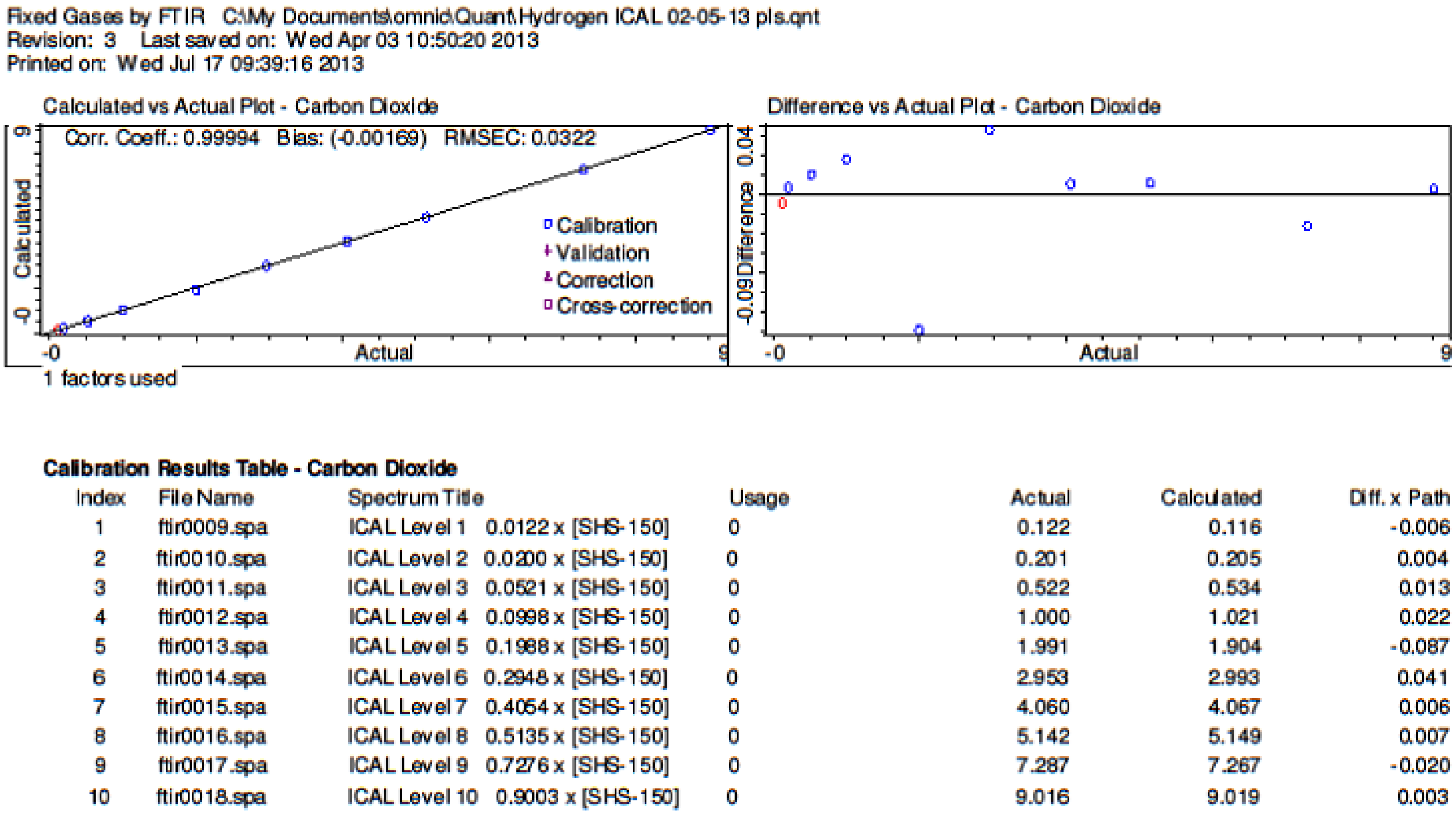
Fixed Gases by FTIR   C:\My Documents\omnic\Quant\Hydrogen ICAL 02-05-13 pls.qnt
Revision: 3   Last saved on: Wed Apr 03 10:50:20 2013
Printed on: Wed Jul 17 09:39:16 2013

Calibration Results Table - Carbon Monoxide

Index	File Name	Spectrum Title	Usage	Actual	Calculated	Diff. x Path
1	ftir0009.spa	ICAL Level 1 0.0122 x [SHS-150]	0	-100.000	0.025	-100.000
2	ftir0010.spa	ICAL Level 2 0.0200 x [SHS-150]	0	-100.000	0.031	-100.000
3	ftir0011.spa	ICAL Level 3 0.0521 x [SHS-150]	0	0.052	0.063	0.011
4	ftir0012.spa	ICAL Level 4 0.0998 x [SHS-150]	0	0.100	0.100	0.001
5	ftir0013.spa	ICAL Level 5 0.1988 x [SHS-150]	0	0.199	0.188	-0.011
6	ftir0014.spa	ICAL Level 6 0.2948 x [SHS-150]	0	0.295	0.297	0.002
7	ftir0015.spa	ICAL Level 7 0.4054 x [SHS-150]	0	0.406	0.399	-0.007
8	ftir0016.spa	ICAL Level 8 0.5135 x [SHS-150]	0	0.514	0.514	0.000
9	ftir0017.spa	ICAL Level 9 0.7276 x [SHS-150]	0	0.729	0.733	0.004
10	ftir0018.spa	ICAL Level 10 0.9003 x [SHS-150]	0	0.902	0.902	0.001

Source: DMS Hydrogen Laboratory

Figure 22: FTIR Calibration Report for Carbon Dioxide



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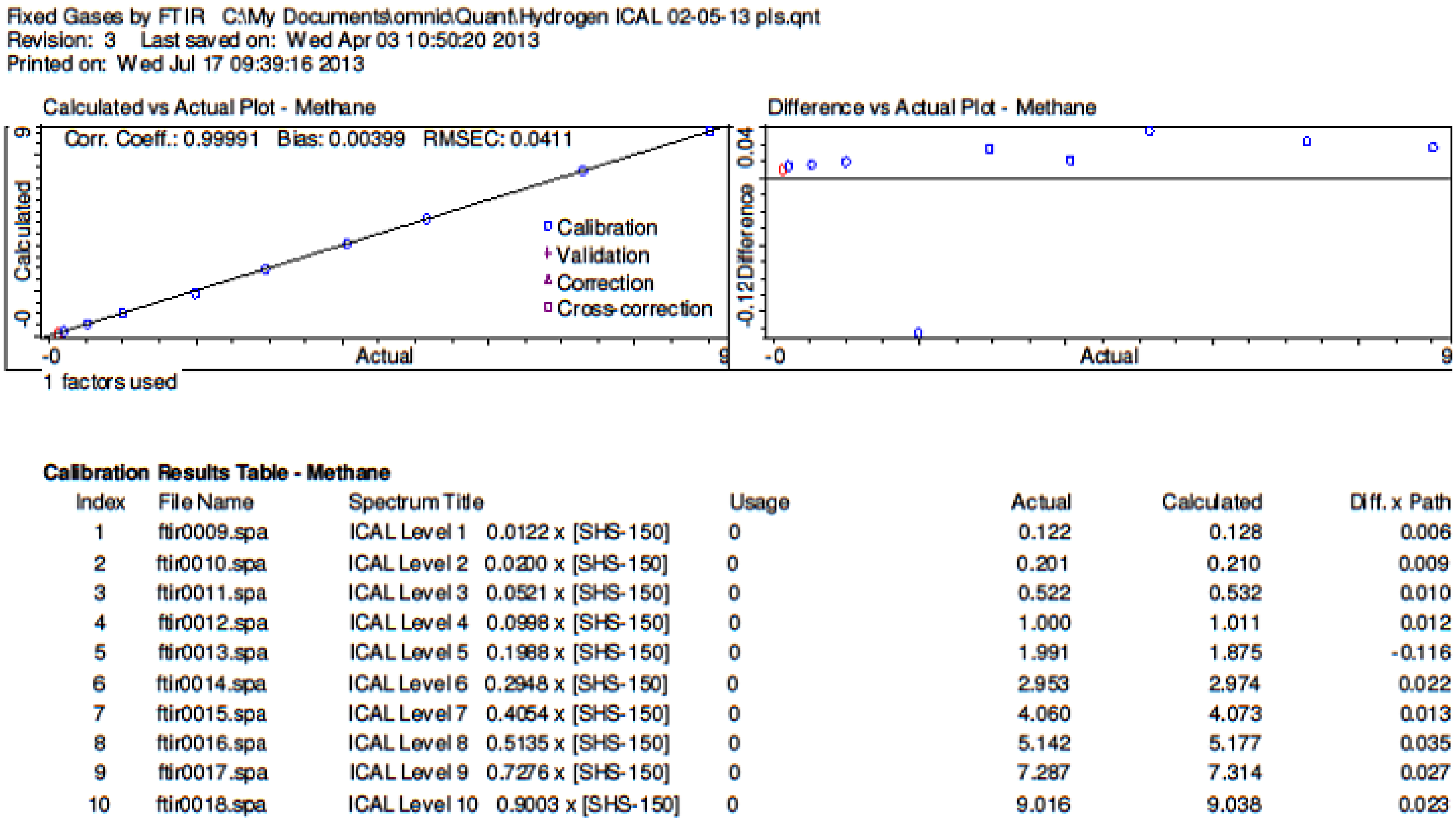
Revision: 3 Last saved on: Wed Apr 03 10:50:20 2013
Printed on: Wed Jul 17 09:39:16 2013

Calibration Results Table - Carbon Dioxide

Index	File Name	Spectrum Title	Usage	Actual	Calculated	Diff. x Path
1	ftir0009.spa	ICAL Level 1 0.0122 x [SHS-150]	0	0.122	0.116	-0.006
2	ftir0010.spa	ICAL Level 2 0.0200 x [SHS-150]	0	0.201	0.205	0.004
3	ftir0011.spa	ICAL Level 3 0.0521 x [SHS-150]	0	0.522	0.534	0.013
4	ftir0012.spa	ICAL Level 4 0.0998 x [SHS-150]	0	1.000	1.021	0.022
5	ftir0013.spa	ICAL Level 5 0.1988 x [SHS-150]	0	1.991	1.904	-0.087
6	ftir0014.spa	ICAL Level 6 0.2948 x [SHS-150]	0	2.953	2.993	0.041
7	ftir0015.spa	ICAL Level 7 0.4054 x [SHS-150]	0	4.060	4.067	0.006
8	ftir0016.spa	ICAL Level 8 0.5135 x [SHS-150]	0	5.142	5.149	0.007
9	ftir0017.spa	ICAL Level 9 0.7276 x [SHS-150]	0	7.287	7.267	-0.020
10	ftir0018.spa	ICAL Level 10 0.9003 x [SHS-150]	0	9.016	9.019	0.003

Source: DMS Hydrogen Laboratory

Figure 23: FTIR Calibration Report for Methane



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Revision: 3   Last saved on: Wed Apr 03 10:50:20 2013
Printed on: Wed Jul 17 09:39:16 2013

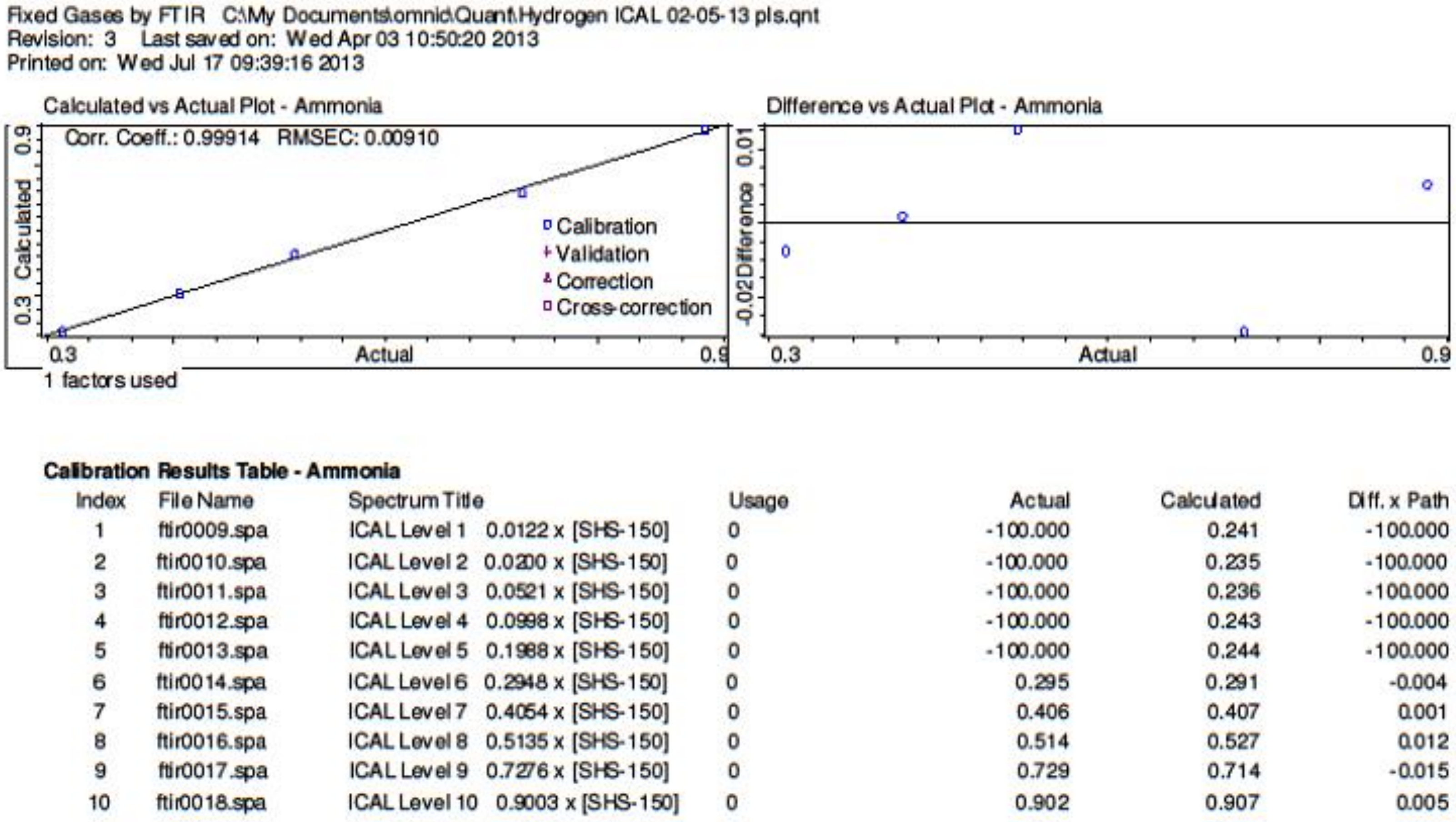
Corr. Coeff.: 0.99991   Bias: 0.00399   RMSEC: 0.0411

Calibration Results Table - Methane

Index	File Name	Spectrum Title	Usage	Actual	Calculated	Diff. x Path
1	ftir0009.spa	ICAL Level 1 0.0122 x [SHS-150]	0	0.122	0.128	0.006
2	ftir0010.spa	ICAL Level 2 0.0200 x [SHS-150]	0	0.201	0.210	0.009
3	ftir0011.spa	ICAL Level 3 0.0521 x [SHS-150]	0	0.522	0.532	0.010
4	ftir0012.spa	ICAL Level 4 0.0998 x [SHS-150]	0	1.000	1.011	0.012
5	ftir0013.spa	ICAL Level 5 0.1988 x [SHS-150]	0	1.991	1.875	-0.116
6	ftir0014.spa	ICAL Level 6 0.2948 x [SHS-150]	0	2.953	2.974	0.022
7	ftir0015.spa	ICAL Level 7 0.4054 x [SHS-150]	0	4.060	4.073	0.013
8	ftir0016.spa	ICAL Level 8 0.5135 x [SHS-150]	0	5.142	5.177	0.035
9	ftir0017.spa	ICAL Level 9 0.7276 x [SHS-150]	0	7.287	7.314	0.027
10	ftir0018.spa	ICAL Level 10 0.9003 x [SHS-150]	0	9.016	9.038	0.023

Source: DMS Hydrogen Laboratory

Figure 24: FTIR Calibration Report for Ammonia



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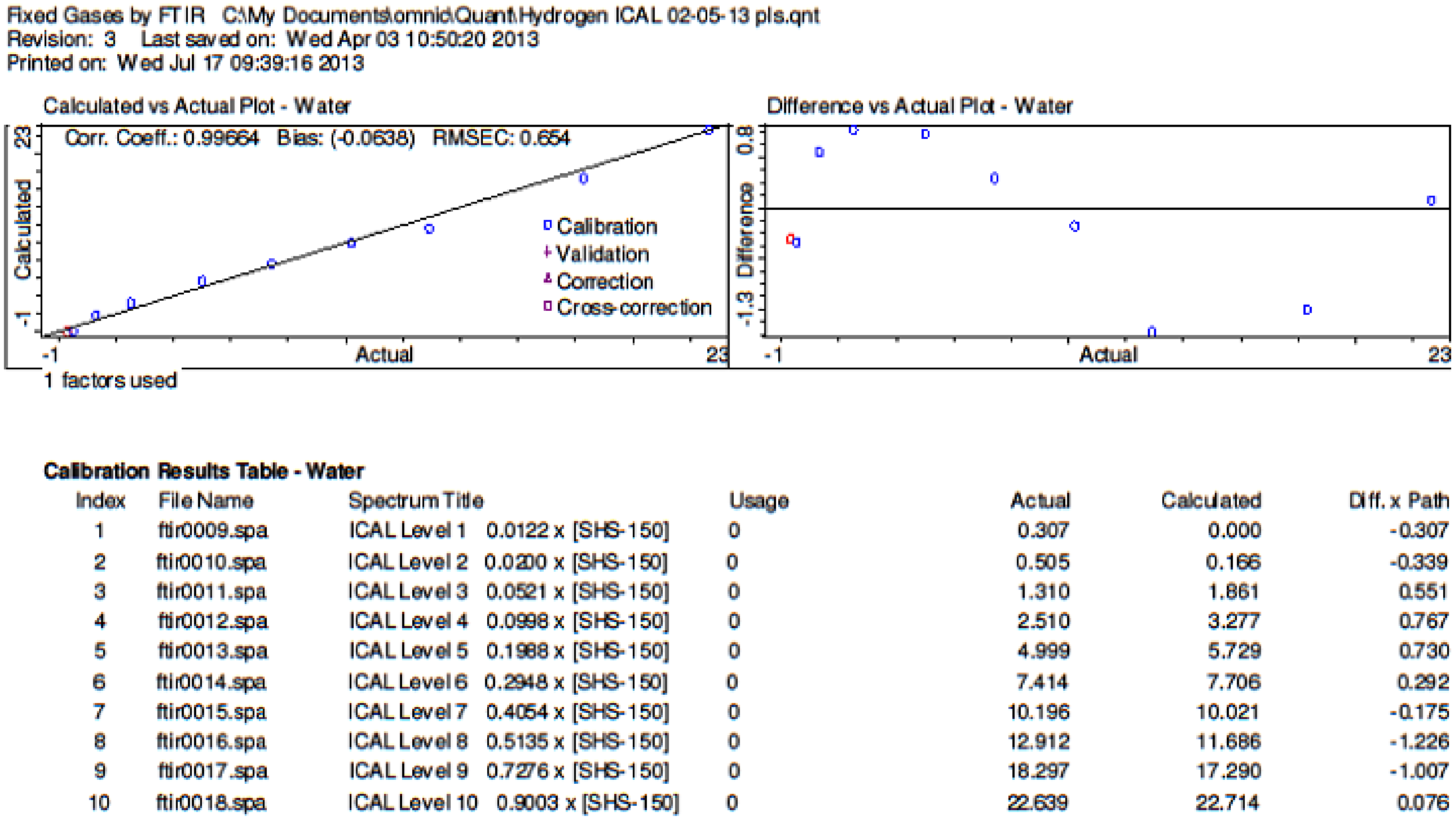
Revision: 3 Last saved on: Wed Apr 03 10:50:20 2013
Printed on: Wed Jul 17 09:39:16 2013

Calibration Results Table - Ammonia

Index	File Name	Spectrum Title	Usage	Actual	Calculated	Diff. x Path
1	ftir0009.spa	ICAL Level 1 0.0122 x [SHS-150]	0	-100.000	0.241	-100.000
2	ftir0010.spa	ICAL Level 2 0.0200 x [SHS-150]	0	-100.000	0.235	-100.000
3	ftir0011.spa	ICAL Level 3 0.0521 x [SHS-150]	0	-100.000	0.236	-100.000
4	ftir0012.spa	ICAL Level 4 0.0998 x [SHS-150]	0	-100.000	0.243	-100.000
5	ftir0013.spa	ICAL Level 5 0.1988 x [SHS-150]	0	-100.000	0.244	-100.000
6	ftir0014.spa	ICAL Level 6 0.2948 x [SHS-150]	0	0.295	0.291	-0.004
7	ftir0015.spa	ICAL Level 7 0.4054 x [SHS-150]	0	0.406	0.407	0.001
8	ftir0016.spa	ICAL Level 8 0.5135 x [SHS-150]	0	0.514	0.527	0.012
9	ftir0017.spa	ICAL Level 9 0.7276 x [SHS-150]	0	0.729	0.714	-0.015
10	ftir0018.spa	ICAL Level 10 0.9003 x [SHS-150]	0	0.902	0.907	0.005

Source: DMS Hydrogen Laboratory

Figure 25: FTIR Calibration Report for Water



Fixed Gases by FTIR C:\My Documents\omnic\Quant\Hydrogen ICAL 02-05-13 pls.qnt
Revision: 3 Last saved on: Wed Apr 03 10:50:20 2013
Printed on: Wed Jul 17 09:39:16 2013

Calibration Results Table - Water

Index	File Name	Spectrum Title	Usage	Actual	Calculated	Diff. x Path
1	ftir0009.spa	ICAL Level 1 0.0122 x [SHS-150]	0	0.307	0.000	-0.307
2	ftir0010.spa	ICAL Level 2 0.0200 x [SHS-150]	0	0.505	0.166	-0.339
3	ftir0011.spa	ICAL Level 3 0.0521 x [SHS-150]	0	1.310	1.861	0.551
4	ftir0012.spa	ICAL Level 4 0.0998 x [SHS-150]	0	2.510	3.277	0.767
5	ftir0013.spa	ICAL Level 5 0.1988 x [SHS-150]	0	4.999	5.729	0.730
6	ftir0014.spa	ICAL Level 6 0.2948 x [SHS-150]	0	7.414	7.706	0.292
7	ftir0015.spa	ICAL Level 7 0.4054 x [SHS-150]	0	10.196	10.021	-0.175
8	ftir0016.spa	ICAL Level 8 0.5135 x [SHS-150]	0	12.912	11.686	-1.226
9	ftir0017.spa	ICAL Level 9 0.7276 x [SHS-150]	0	18.297	17.290	-1.007
10	ftir0018.spa	ICAL Level 10 0.9003 x [SHS-150]	0	22.639	22.714	0.076

Source: DMS Hydrogen Laboratory

The MDL is a calculated value based on a minimum of seven replicate analyses of a low-level standard at a 95 percent confidence interval. The calculated MDLs shown in the tables above may need to be adjusted when real samples are analyzed because of matrix and other effects. Using these calibrations, a method detection limit study was performed for carbon dioxide, carbon monoxide, methane, and ammonia, following the criteria outlined in 40 CFR136 Appendix D. The results of this study are shown in Tables 21 – 24.

Table 21: MDL for CO_2 in Hydrogen by FTIR

Sample	**Pressure**	**Conc.**	**Calc. Conc.**	**Diff.**
1	1067.3	0.01977	0.055	0.0352
2	1065.2	0.01977	0.056	0.0362
3	1068.3	0.01977	0.054	0.0342
4	1067.7	0.01977	0.052	0.0322
5	1069.4	0.01977	0.051	0.0312
6	1066.8	0.01977	0.053	0.0332
7	1070.5	0.01977	0.052	0.0322
8	1067.8	0.01977	0.065	0.0452
9	1066	0.01977	0.056	0.0362
10	852.6	0.01977	0.054	0.0342
		Mean:	0.0548	0.0350
		Std. Dev.:	0.0040	0.0040
		Variance:	< 0.0001	< 0.0001
		MDL:	0.011	

Source: DMS Hydrogen Laboratory

The FTIR studies have concluded that CO, CO_2, and methane can be reliably identified and quantified at the required levels. Instrument detection limits were determined in accordance with procedures outlined in U.S. EPA 40 CFR 401.13 subsection 136 Appendix D.

Ammonia was spiked in the MDL standard at 0.396 ppm, and had a calculated MDL of 0.138, which is higher than the limit set in *SAE J2719*. This calculated MDL does not correlate with reality; ammonia was not detected on the instrument below 0.291 ppm. Ammonia and water vapor are both detectable by FTIR but this method is not sensitive enough for the quantification of these contaminants at the levels required by *SAE J2719*. CRDS has been shown to be sufficiently sensitive for the determination of ammonia in hydrogen fuel and is a promising alternative method for this analysis.

Table 22: MDL for CO in Hydrogen by FTIR

Sample	Pressure	Conc.	Calc. Conc.	Diff.
1	1067.3	0.0742	0.103	0.0288
2	1065.2	0.0742	0.095	0.0208
3	1068.3	0.0742	0.100	0.0258
4	1067.7	0.0742	0.113	0.0388
5	1069.4	0.0742	0.111	0.0368
6	1066.8	0.0742	0.110	0.0358
7	1070.5	0.0742	0.111	0.0368
8	1067.8	0.0742	0.102	0.0278
9	1066	0.0742	0.101	0.0268
10	852.6	0.0742	0.093	0.0188
		Mean:	0.104	0.030
		Std. Dev.:	0.0070	0.0070
		Variance:	0.0000	0.0000
		MDL:	0.020	

Source: DMS Hydrogen Laboratory

Table 23: MDL for Methane in Hydrogen by FTIR

Sample	Pressure	Conc.	Calc. Conc.	Diff.
1	1067.3	0.0989	0.193	0.0941
2	1065.2	0.0989	0.185	0.0861
3	1068.3	0.0989	0.192	0.0931
4	1067.7	0.0989	0.164	0.0651
5	1069.4	0.0989	0.169	0.0701
6	1066.8	0.0989	0.181	0.0821
7	1070.5	0.0989	0.195	0.0961
8	1067.8	0.0989	0.159	0.0601
9	1066	0.0989	0.160	0.0611
10	852.6	0.0989	0.158	0.0591
		Mean:	0.176	0.077
		Std. Dev.:	0.0152	0.0152
		Variance:	0.0002	0.0002
		MDL:	0.044	

Source: DMS Hydrogen Laboratory

Table 24: MDL for NH3 in Hydrogen by FTIR

Sample	Pressure	Conc.	Calc. Conc.	Diff.
1	1067.3	0.3955	0.325	-0.0705
2	1065.2	0.3955	0.386	-0.0095
3	1068.3	0.3955	0.441	0.0455
4	1067.7	0.3955	0.448	0.0525
5	1069.4	0.3955	0.475	0.0795
6	1066.8	0.3955	0.434	0.0385
7	1070.5	0.3955	0.470	0.0745
8	1067.8	0.3955	0.410	0.0145
9	1066	0.3955	0.466	0.0705
10	852.6	0.3955	0.474	0.0785
		Mean:	0.433	0.037
		Std. Dev.:	0.0478	0.0478
		Variance:	0.0023	0.0023
		MDL:	0.138	

Source: DMS Hydrogen Laboratory

Table 25: MDLs and Proposed Reporting Limits for FTIR Analytes

Analyte	MDL	Proposed RL	***SAE* J2719 limit**
CO	0.0204 ppm	0.200 ppm	0.2 ppm
CO_2	0.0115 ppm	2.000 ppm	2 ppm
Methane	0.0439 ppm	2.000 ppm	2 ppm
Ammonia	0.1385 ppm	0.100 ppm *	0.1 ppm
Water	indeterminate	5.00 ppm **	5 ppm

* MDL > RL

** Results too variable for MDL determination

Source: DMS Hydrogen Laboratory

CRDS: Determination of H_2O, NH_3, and Formaldehyde

Because of the problems encountered with ammonia and water analysis by FTIR, CRDS was evaluated as an alternative method for the determination of these analytes. As described in the Cavity Ring Down Spectrometer section above, CRDS uses the decay time of a laser pulse tuned to the analyte of interest to calculate the concentration of the analyte based on its extinction coefficient and the volume of the sample. CRDS makes an absolute determination of concentration based on Beer’s Law, and so does not require any calibration.

CRDS was demonstrated successfully for water and ammonia. A standard for formaldehyde was not available, so evaluation of CRDS for the determination of formaldehyde was not done.

Field Sampling of Hydrogen Fuel at Dispensers

In November 2013, hydrogen fuel samples were collected from five of the public stations in California. Figure 26 shows DMS Staff Environmental Scientist John Mough collecting a sample using the Hydrogen Fuel Quality Sampling Apparatus discussed in the Sampling Apparatus and Method section. The dispenser nozzle is seen connected to the sampling apparatus. The orange coil at the bottom of the photograph is the connection grounding the dispenser to the sampling apparatus. The hose leading from the left side of the apparatus is connected to the vent stack (not shown) that releases hydrogen from the apparatus at a safe height above the ground.

These field samples were successfully analyzed using the methods discussed above. Four of the samples had no detectable contaminants. Several contaminants were found in the sample from the fifth station. After reviewing the DMS data, that station shut down its dispenser for an investigation, and took corrective action to resolve the issues found.

Figure 26: Field Collection of Hydrogen Fuel Quality Sample

Source: DMS Hydrogen Laboratory

1.4 Summary, Discussion, and Future Work

Project Summary

A basis for a robust and reliable scheme for the analysis of hydrogen fuel quality for the specifications of *SAE J2719* has been developed. The methods presented in the Production of Hydrogen section, when run in combination, provide for the determination of most of the *SAE J2719* analytes with the required sensitivity. Table 26 summarizes the methods and detection limits that have been validated by DMS.

Table 26: DMS Validated Methods and MDLs

Analyte	Analytical Method	*SAE J2719* Limit (ppm)	DMS MDL (ppm)
Total hydrocarbons*	GC-FID (System 2) and FTIR	2	0.012
Helium	GC-TCD (System 2)	300	20
Nitrogen	GC-PDHID (System 2)	100	11
Argon	GC-PDHID (System 2)	100	11
Carbon dioxide	GC-FID (System 2) and FTIR	2	0.23 (FID) 0.011 (FTIR)
Carbon monoxide	FTIR	0.2	0.020
Sulfur compounds	GC-PFPD (System 1)	0.004	0.0106 - 0.0071 **
Total halogenates	GC/MS (System 1)	0.05	†

** As listed in Table 12, each sulfur compound tested had a different MDL. The *SAE J2719* maximum concentration of 0.004 ppm is ambiguous since it does not specify a reference compound or response factor to be used in MDL calculations. Therefore, the range of values listed in Table 12 is reported in Table 26. These results will be presented to SAE for use in revising the sulfur contaminant specification in *SAE J2719*.

† Because of time limitations, MDL studies for all of the halogenates were not completed. However, the sensitivity of the GC/MS analysis is expected to be adequate to meet the specifications of *SAE J2719* for all compounds.

Source: DMS Hydrogen Laboratory

The set of methods listed in Table 26 comprise a practical scheme for the analysis of hydrogen fuel quality. However, this list is not intended to be exhaustive or exclusive. It should not be interpreted to imply that other analytical methods and detector combinations are not equally feasible. The work described in this report should provide a useful starting point for others in this field.

Method development for several of the *SAE J2719* analytes is incomplete. In some cases, different analytical approaches will be required. Analytes needing additional work are shown in Table 27, along with possible alternative methods for their analysis. The analytes listed in Table 27 are discussed in more detail in Section Considerations for Future Work.

Table 27: *SAE J2719* Analytes Requiring Additional Work

Analyte	Proposed Analytical Method(s)	*SAE J2719* Limit (ppm)
Water	CRDS	5
Ammonia	CRDS	0.1
Formaldehyde	CRDS	0.01
Formic acid	GC/MS	0.2
Oxygen	ECD, GC/MS, CRDS	5

Source: DMS Hydrogen Laboratory

Considerations for Future Work

Water:

CRDS has been shown to have sufficient sensitivity for the specifications of *SAE J2719* for water and ammonia. However, the precision of the method for these analytes has not been established. Therefore, water is listed in Table 27. Since CRDS is a direct measurement method that does not depend on a calibration, useable data can generate on samples even though this method has not been fully validated.

Ammonia:

Neither FTIR nor IC was successful for the analysis of ammonia. While ammonia can be seen by FTIR, the detection limit of the instrument as configured and tested at DMS did not meet the specification of *SAE J2719*. IC was found to be unsuitable for ammonia in spite of its extremely high sensitivity because a robust and reliable method to transfer the analyte to the liquid IC eluant could not be developed.

FTIR might be used to confirm high levels of ammonia. With the issue of water in the reference hydrogen gas resolved, the detection limit for ammonia by FTIR could be determined.

CRDS has been shown to have sufficient sensitivity for the specifications of *SAE J2719* for ammonia. A validation for ammonia could not be completed because of the issue of water contamination in the reference hydrogen gas. Since this issue has been resolved, it is expected that a satisfactory validation can be done.

Formic Acid and Formaldehyde:

The problems encountered with the IC for ammonia would also occur in the determination of formic acid and formaldehyde. A CRDS module for formaldehyde is expected to be sensitive enough to meet the specification of *SAE J2719* and has been procured. However, a commercial standard of formaldehyde in hydrogen is not available. A permeation tube is needed to prepare calibration standards for formaldehyde as was done for the sulfur compounds. CRDS is not applicable to formic acid at this time.

GC/MS analysis of formic acid and formaldehyde is possible but may not have enough sensitivity to meet the specifications of *SAE J2719*. It should be possible to validate the determination of by GC/MS and include these analytes with the halogenated compounds. A means of preparing calibration standards for formic acid in hydrogen must be validated before a method can be developed.

If the issue of background water interference in the FTIR can be resolved, this method may be applicable to the determination of formaldehyde, and formic acid as well as ammonia. This would be worth pursuing in order to have confirmation methods for these analytes included in the analytical scheme. If analysis by FTIR is found to be sensitive enough, it could possibly eliminate the need for a re-analysis of a sample in which one or more contaminants was identified at levels above *SAE J2719* limits.

Oxygen:

GC-ECD has been shown to have adequate sensitivity for the determination of oxygen in hydrogen fuel. However, the reproducibility from injection to injection was unacceptable. Additional laboratory work in consultation with the detector manufacturer might resolve this problem. Recently, a CRDS module for oxygen has been introduced. In view of the successful application of CRDS to the determination of water and ammonia, this is a potential alternative method for the determination of oxygen in hydrogen.

Particulates:

In Sept 2010, ASTM published test method *ASTM D7650 - 10 Standard Test Method for Sampling of Particulate Matter in High Pressure Hydrogen used as a Gaseous Fuel with an In-Stream Filter*. With an approved test method in place, no work on particulate determination was done for this project. If particulates are found in hydrogen fuel sold in California, it may be necessary to evaluate method *D7650 – 10.*

Summary of DMS Methods for Hydrogen Fuel Analysis

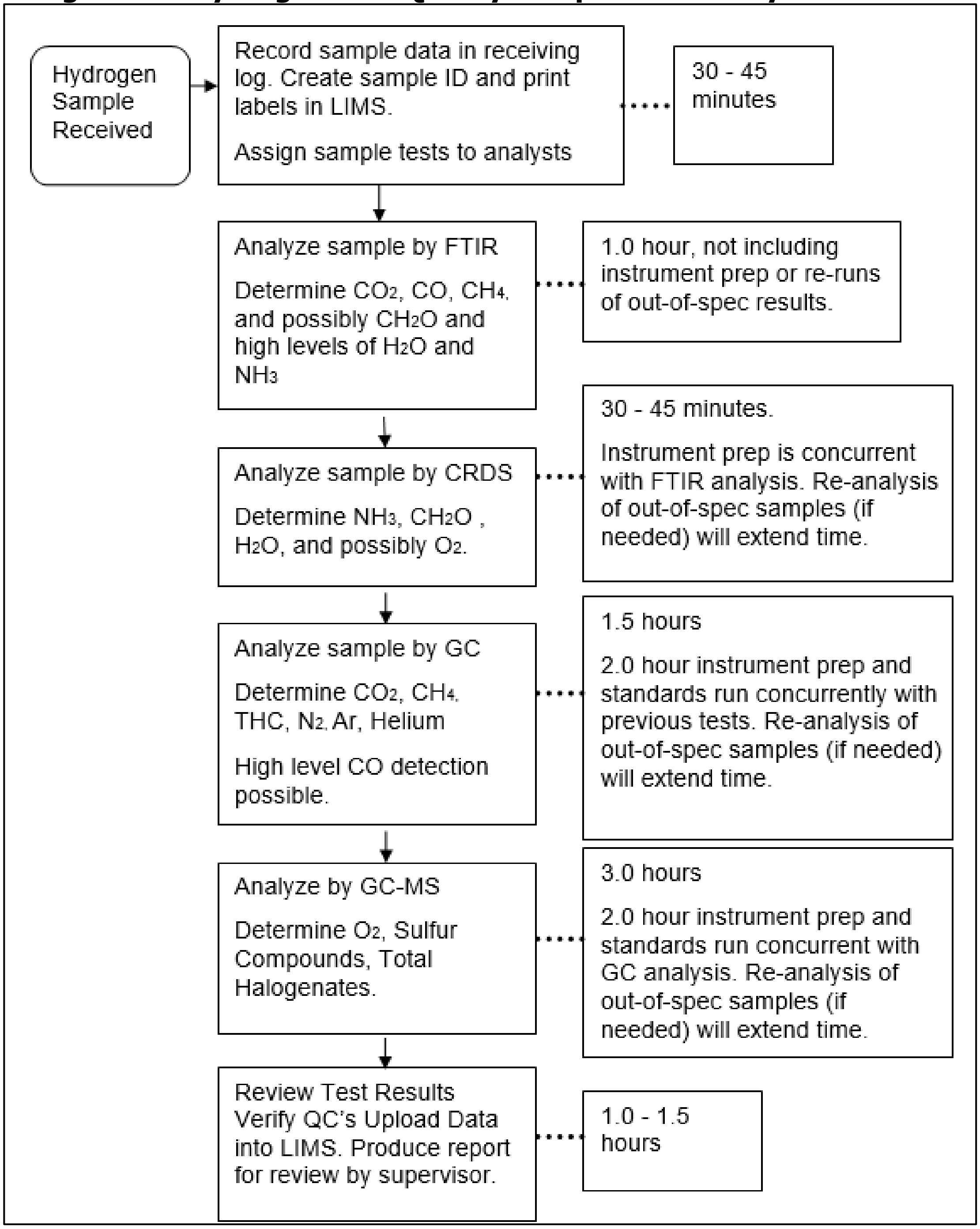
Analysis of hydrogen fuel sampled at a commercial dispenser might be expected to show particulate contamination arising from environmental contamination and repeated use of the nozzle assembly by customers. An analysis of particulates in a hydrogen sample could result in false positives, disrupting the sale of fuel. A previous proposal to incorporate a particle filter in the vehicle fuel line may be a preferable approach.

The full-profile analysis of hydrogen gas for fuel cells requires multiple instruments and methods to quantify all potential actionable impurities in the sample gas matrix. Not all potential contaminants of concern are likely to be present in a given hydrogen source and industry producers may want to focus on testing and addressing impurities common to their particular hydrogen production process.

For normal production work at DMS, up to six samples can be completed in about a day and a half with the GC-MS running overnight. Throughput is limited by the capacity of the sample switching assembly to connect the canisters to each instrument in turn.

To minimize the amount of fuel sample used in testing, only one canister is used for a given sample. This minimizes the cost of samples taken for testing. The sample switching assembly must be moved manually between instrument systems to the next to complete the testing. Figure 27 shows a schematic flow chart for sample in the DMS laboratory.

Figure 27: Hydrogen Fuel Quality Sample Laboratory Flow Chart



Source: DMS Hydrogen Laboratory

Lessons Learned

In the course of this work, many lessons were learned that might be of value to other analysts. These are presented here.

Reference Hydrogen Quality

Ultra-high purity hydrogen (0.99999 or better) is required as a matrix for calibration standards and a reference for instrument blanks. Cylinders of ultra-high purity Hydrogen are readily available from many suppliers; however, experience at DMS has shown that contamination of cylinders with water (and possibly other substances) does occur. Quality verification of all ultra-high purity hydrogen received, especially for water content, is an essential first step in achieving acceptable analytical results.

Out-of-specification reference hydrogen containing water will interfere with the CRDS used for the determination of ammonia and formaldehyde. The CRDS provides a convenient method to ensure that an excessive concentration of water is not present in the reference hydrogen gas.

Argon Purity for the Determination of Helium

Helium in hydrogen is determined by GC-TCD with argon as a carrier gas. Early tests showed baseline variability in the TCD detector baseline that altered the integration of the helium peak from sample to sample. Frequently a negative peak was displayed at the elution point of helium. It was determined that trace helium was present in the argon carrier gas at levels greater than prepared standards. Cylinder argon was replaced with a Dewar supply of liquid argon to generate the reference gas. This stabilized the baseline and eliminated negative peaks in the helium chromatogram.

Consideration for GC Inlet Design

Field samples of hydrogen fuel are collected and analyzed at much higher pressures than the laboratory samples and standards used for method development and calibration. All analytical instruments require high pressure sample inlets and selector valves rated for at least 1800 psi, the rated pressure of the high-pressure sample containers used for this work. To meet this requirement, an upgrade of a standard GC inlet is needed.

Cleaning and baking out of columns in the GC of System 2 required extensive labor as the maximum temperature rating for the of the Hayesep N® is much lower than the ideal bake-out temperature for the molecular sieve columns. This meant that regenerating the molecular sieves required the removal of the Hayesep N® columns. Reassembling all of the connectors in the system was challenging and time-consuming because of the leaks introduced.

To address these issues, a redesigned GC system was added. It was equipped with a sample selector valve rated for high pressures and step-down regulator. In addition, separate column ovens and thermal controls for the Hayesep N® and the molecular sieve columns were included to make system maintenance easier.

FTIR Sensitivity to Ambient Water Vapor

The FTIR is highly sensitive to moisture and atmospheric contaminants. A high-volume continuous purge of filtered dry nitrogen is required to maintain a clean optical bench for the instrument. Heating sample lines and sample ovens are also necessary to minimize moisture accumulation in the sampling system and reduce interferences from water vapor. However, even with these measures taken, a background sufficiently clean for the analysis of ammonia in hydrogen fuel could not be achieved by the DMS laboratory. FTIR is an attractive technique for hydrogen fuel quality analysis since it is very sensitive to so many of the SAE *J2917* contaminants. A practical means of further reducing the background from ambient water vapor would permit more analytes to be determined by FTIR and provide analytical confirmation without a need to rerunning a sample.

IC/CD Issues

The analysis of ammonia by IC/CD requires its transformation into ammonium ion in solution. While the detection limits and sensitivity were excellent with this instrument, the quantitative trapping and conversion of ammonia from the gas phase to solution was not successful in spite of repeated efforts. The variability in recovery does not support the required level of confidence in the measured results. In spite of the extremely high sensitivity of the IC/CD, it does not appear to be applicable to the analysis of hydrogen fuel.

CRDS

Water vapor detection in hydrogen gas is both reliable and robust with this relatively new technology. Analysis of other analytes such as ammonia, formaldehyde, and oxygen are also possible with CRDS. However, the presence of water above specified concentrations can interfere with the determination of other analytes. Water levels above 10 ppm invalidate any reading for formaldehyde and water levels above 15 ppm invalidate the readings for ammonia. Therefore, it is essential to establish that a sample meets the SAE *J2719* specification for water before analyses known to be susceptible to water interference are run.

CHAPTER 2: Hydrogen Measurement Standard

Existing California statutes and regulations govern the commercial sale of all transportation fuels in California to protect consumers and ensure a level playing field among suppliers. Fuel dispensers for commercial refueling stations must be *type evaluated* by the CDFA/DMS to insure they meet all required metrological specifications. Currently, no hydrogen fuel dispensers have been approved for retail use in California. The direct sale of hydrogen fuel to consumers requires the development of standards and procedures specifically to test and approve hydrogen fuel dispensers at retail outlets. The work described in this report was undertaken to fill this need.

The first phase of this project was the development of specifications, tolerances, and a method of sale requirement for the commercial measurement of hydrogen fuel delivery equipment. In the United States, this is a multi-step process. It starts with the development of model regulatory language by the National Conference on Weights and Measures (NCWM). The Conference is a consensus organization whose membership is open to Federal, state, and local weights and measures officials, equipment manufacturers, industry representatives, and any other interested parties.

In response to a recognized need for new regulations to address changes in technology and marketplace conditions, the NCWM Specifications and Tolerances Committee meets to reach consensus on model language. This language is then published by the U.S. Department of Commerce National Institute of Standards and Technology (NIST) in its *Handbook 44: Specifications and Tolerances and Other Technical Requirements for Weighing and Measuring Devices.* States may then adopt this code in their law or regulations. The staff of the CDFA played a leading role in the development of the model language needed for hydrogen regulations. The latest version of NIST *Handbook 44* is automatically adopted each year by reference in Division 5 of the California Business and Professions Code (BPC). The CDFA has proposed modifications to the language in *Handbook 44* for California*.* Procedures for type evaluation and field testing of hydrogen dispensers have also been developed. Type evaluation is the process used to evaluate new weighing and measuring devices for accuracy, precision, reliability, and compliance with all applicable codes and regulations. Type evaluation is required before a new device can legally be used in commerce.

With the necessary regulatory language in place, the following step in the project was the fabrication and evaluation of reference standards for testing of hydrogen dispensers. Three standards, gravimetric, volumetric, and master meter, were incorporated into one device for field testing. This device was designed and constructed under an agreement with the National Renewable Energy Laboratory (NREL) in Golden, Colorado. After testing, the gravimetric standard met the required tolerances and was accepted for use by the CDFA for type evaluation and field testing. The volumetric and master meter standards did not meet the required tolerances and will be used only for data collection.

2.1 Introduction and Overview

Metrology and Transportation Fuels in California

From the earliest times, accepted standards of weight and volume were needed to support equitable trade and combat fraud. Such standards remain vital to commerce in today's world.

Metrology, the science of measurement, encompasses all that is necessary for the accuracy and precision of measurements to be reliable and accepted in commercial transactions. Metrology is essential to the maintenance of a fair and transparent marketplace today.

There are three components to any measurement: a unit of measure, the quantity determined by the measurement, and the uncertainty associated with the measurement. In commercial transactions, each of these components is subject to regulation for the protection of both buyers and sellers. Many measurements must be codified to support public health and safety, consumer protection, and to provide a level playing field for commercial activity. These aspects of measurement science make up the field of metrology.

NIST defines metrology as "the practice and process of applying regulatory structure and enforcement" to measurements. [23] Metrology creates a regulatory framework through which all parties can rely on the accuracy and reliability of commercial measurements. These measurements are made according to established procedures and specifications. The units and devices used are traceable to recognized international standards and meet accepted specifications. Adherence to the principles and protocols of metrology by sellers, buyers, and regulators supports transparent and equitable trade and commerce. Metrology codes and standards are written to ensure the accuracy of commercial measurements, enhance consumer protection, foster competition, and facilitate state and national economic growth and trade.

BPC Division 5, Chapter 14 (Petroleum) assigns oversight of the retail sale of transportation fuels in California to CDFA. In 2005, Senate Bill 76 (Statutes of 2005, Chapter 91) amended BPC Section 13401 to add hydrogen as a motor vehicle fuel. Through this amendment, all codes and regulations for the retail sale of motor vehicle fuels apply to hydrogen fuel. A link to the text of the BPC sections relating to the regulation of fuels may be found in Appendix F.

BPC, Section 12500.5 requires that commercial fuel dispensing devices be approved by DMS through the California Type Evaluation Program.[24] The California Type Evaluation Program defines type evaluation as "The examination of a weighing or measuring instrument for the legal purpose of certifying that its design and performance complies with all applicable weights and measures requirements."[24] A motor fuel dispenser must receive a Certificate of Approval from DMS before it may be used in commerce in California. BPC Section 12107 further requires that the requirements for commercial fuel dispensing devices be adopted by reference to model codes published by the NIST in its *Handbook 44 Specifications Tolerances, and Other Technical requirements for Weighing and Measuring Devices***.** With the inclusion of hydrogen as a motor vehicle fuel in BPC Section 13401, commercial hydrogen dispensers are subject to the requirements of BPC Sections 12500.5 and 12107.

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[23] International Legal Metrology Program Webpage: http://www.nist.gov/pml/wmd/ilmg/index.cfm accessed 1/10/2020; For more information on legal metrology, see *OIML D 1 2012 Considerations for a Law on Metrology*, issued by the intergovernmental International Organization of Legal Metrology, http://www.oiml.org/en/files/pdf_d/d001-e12.pdf, accessed Jan 10, 2020.

[24] California Type Evaluation Program information: http://cdfa.ca.gov/dms/programs/ctep/ctep.html, accessed Jan 10, 2020.

Prior to 2007, no specifications or tolerances for hydrogen fuel dispensers had been developed. In such situations, *NIST Handbook 44* provides procedures for the approval of unclassified devices. However, without device-specific protocols, manufacturers face uncertainty about the requirements that a weights and measures official might impose on a device. Because of this uncertainty, and the limited market for commercial hydrogen dispensers, device manufacturers have been reluctant to invest in obtaining type approval for hydrogen dispensers. To date, no retail hydrogen fuel dispensers have been approved for commercial use in California. The work described in this report was undertaken to develop the standards and procedures needed for the testing and evaluation of hydrogen dispensers.

Fuel Cell Vehicles in California

California faces continuing challenges in achieving clean air and an adequate and sustainable energy supply. The State has set the following goals:

- A reduction in GHG emissions to 80 percent below 1990 levels by 2050.[1] [25]
- A decrease in petroleum fuels usage to 15 percent below 2003 levels by 2020[26]
- An increase in the use of alternative transportation fuels to 20 percent of all fuel consumed by 2020 and 30 percent by 2030[3]
- A reduction of emissions of NO_x to 80 percent of 2010 levels by 2023 to meet current Federal ozone standards[27]

New technologies and new approaches in many areas are needed to meet these challenges. The CEC’s Clean Transportation Program was created in 2007 to support innovation in the transportation sector. This program was established by Assembly Bill 118 (Núñez, Chapter 750, Statutes of 2007) and subsequent amendments. The development of FCEVs is one of the efforts supported by this program.

Fuel cells are clean and efficient sources of energy that have found a wide range of applications. Fuel cells use the electrochemical reaction of oxygen and hydrogen to generate electricity. Such electrochemical reactions are much more energy efficient than the combustion of petroleum fuels. FCEVs have no tailpipe emissions of GHGs or NO_x. Water and a small amount of heat are the only by-products of fuel cells, eliminating pollution from tailpipe emissions at the point of use. Expanded use of hydrogen as a transportation fuel will reduce the state’s dependence on petroleum, reduce toxic tailpipe emissions, and help meet alternative fuel goals. Hydrogen FCEVs will play an essential role in reaching California’s goal of a sustainable energy supply.

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[25] ARB Climate Change Programs on the ARB Website: http://www.arb.ca.gov/cc/cc.htm, accessed Jan 9, 2020; California Office of the Governor, Arnold Schwarzenegger Executive Order S-3-05, June 1, 2005; California Office of the Governor, Arnold Schwarzenegger Executive Order S-3-05, June 1, 2005.

[26] *Reducing California’s Petroleum Dependence*, ARB and CEC joint agency report publication #P600-03-005, August 2003.

[27] *Vision for Clean Air: A Framework for Air Quality and Climate Planning*, Public Review Draft CARB, the South Coast Air Quality Management District and the San Joaquin Valley Unified Air Pollution Control District, page 10, June 27, 2012. http://www.arb.ca.gov/planning/vision/docs/vision_for_clean_air_public_review_draft.pdf, accessed Jan 10, 2020.

Growing numbers of transit systems throughout California are using fuel cell buses. Large numbers of fuel cell forklifts and similar vehicles are in use in industrial and warehouse settings. A limited number of fuel cell passenger cars are currently leased to consumers in California by manufacturers in demonstration programs. In response to mandates to increase fleet fuel efficiency and decrease tailpipe emissions, many major automakers plan to begin commercial sale of FCEVs in California in 2015 – 2017.

Highlights of the history of hydrogen fuel and fuel cell vehicles are presented in the Time Line in Appendix A.

Properties of Hydrogen and Safety Considerations

Hydrogen is the most abundant element in the universe. However, the diatomic molecular form of hydrogen needed to power fuel cells rarely occurs naturally on earth since it is too light to be retained by the Earth's gravitational force. Earth's supply of hydrogen is found in combination with other elements; at the surface, mostly in water bonded to oxygen. Smaller amounts of hydrogen at Earth's surface are found in minerals and other hydrides.

With no terrestrial source of molecular hydrogen, the very high purity hydrogen required by fuel cells must be manufactured, most often from methane by steam reformation:

$$CH_4 + H_2O \rightarrow CO + 3\ H_2$$

Molecular hydrogen can also be produced from water by electrolysis:

$$2\ H_2O \rightarrow 2\ H_2 + O_2$$

These endothermic reactions require an input of energy, some of which is stored in the chemical bond of the hydrogen molecule. In a fuel cell, this stored energy is released as electricity by a reverse reaction:

$$2\ H_2 + O_2 \rightarrow 2\ H_2O$$

Fuel cells are clean and efficient sources of energy that have found a wide range of applications. Hydrogen-powered fuel cell vehicles will have a crucial role in a clean and sustainable energy economy in California and the nation.

Hydrogen has long been used in large quantities in the petroleum, chemical, metallurgy, and food industries. Hydrogen has unique characteristics that require special handling precautions for safety. The safety records of the diverse industrial applications demonstrate that hydrogen need not pose an undue risk as a vehicle fuel. In fact, overall, hydrogen may be safer than conventional petroleum transportation fuels. Vapors of all fuels are flammable within some range of concentrations in air. For hydrogen, this range is roughly 4 – 75 percent. This is quite wide compared to that of conventional petroleum fuels. However, even lower concentrations of gasoline (1 percent), diesel (0.6 percent), and propane (2.2 percent) will support combustion. Both petroleum-based fuels and hydrogen can explode if there are leaks and ignition sources present.

Because of its lighter than air buoyancy, hydrogen will rapidly diffuse upwards in the event of a leak. This is true even if the hydrogen has been ignited. Consequently, hydrogen fires are concentrated, vertical, narrow, and dissipate rapidly. Gasoline and diesel vapors and liquids, on the other hand, are heavier than air. They will remain low and spread along the ground if there is a fuel leak, and seek lower elevations such as basements, creeks, and gullies, increasing the fire risk to the surrounding buildings and objects. In this sense, hydrogen may be considered safer than conventional fuels.

Hydrogen has the highest energy content per unit weight of any element. It is also the lightest element known. As a result, it has a very low energy density under normal ambient conditions. Hydrogen tanks in fuel cell vehicles must be pressurized to 10,000 pounds/ square inch (psi) so that the vehicle can carry enough fuel to achieve an acceptable driving range. The construction of cylinders and tanks for the safe storage and handling of compressed gases is well understood. The principles and safety guidelines already in place for industrial applications can be directly applied to the requirements for infrastructure for the hydrogen fuel industry.

Existing Hydrogen Fuel Infrastructure in California

In late 2013, approximately 125 FCEVs have been leased to Californians by automobile manufacturers for research and testing purposes. Currently, vehicle manufacturers and dealers contract with a limited number of hydrogen station operators to provide refueling to customers as part of their vehicle leases. A similar situation exists in other states where fuel cell vehicles have been introduced.

At least two manufacturers plan to begin retail sales of FCEVs in the state in 2015. Other manufacturers will introduce their FCEV models in 2016 and 2017. California drivers are expected to purchase or lease an estimated 53,000 FCEVs by 2017.[27] Retail sales of FCEVs in California will begin in 2015. The CEC and ARB have forecast that sales will quickly grow to tens of thousands of FCEVs annually. Such rapid acceptance of FCEVs by consumers will depend in large part on the anticipated availability of a network of convenient and reliable hydrogen refueling stations. Drivers are dependent on the highly distributed network of retail outlets for the direct sale of gasoline. The abundance of gasoline stations is largely taken for granted. It is likely that California’s drivers will want the same level of convenience if they purchase a FCEV.

The first adopters of FCEVs are clustered mainly in southern California. Table 28 lists the public hydrogen refueling stations currently operating in the state. Seven are in the greater Los Angeles area, one is in Thousand Palms near Indio, and one is in San Francisco Bay Area city of Emeryville. Seventeen more stations are under development. In addition, thirteen private and demonstration stations are now in operation.[28]

The California Fuel Cell Partnership (CaFCP) is a collaborative group bringing together governmental agencies, energy providers, vehicle manufacturers, and technology companies to promote the commercialization of FCEVs. The CEC, the CARB, and the CDFA are all members of the Partnership. For more information about the CaFCP, contact by e-mail at info@CaFCP.org or visit its website at http://CaFCP.org. The CaFCP maintains an up-to-date list of hydrogen stations in California on its website. This list includes public and demonstration stations, along with locations under development. The list may be accessed at https://cafcp.org/stationmap.

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[28] California Fuel Cell Partnership Q3 2013 Status Report. For a copy of the report, contact the CAFCP:
Phone: (916) 371-2870 Fax: (916) 375-2008 e-mail: info@CaFCP.org.

As described in *A California Road Map*[29], published by the CAFCP, the existing network of hydrogen stations is currently in an emerging, pre-commercial stage sufficient to support the FCEVs on the state's highways. To support the anticipated rapid growth in FCEVs beginning in 2015, a corresponding growth in the hydrogen infrastructure will be needed. *A California Road Map* sets out a practical path to developing this expanded infrastructure. In the first stage, by 2016 the existing refueling station network would be expanded to 68 stations. Most of these would expand the coverage area of the existing clusters of stations. Research and computer modeling by the CaFCP have identified areas where early purchasers of FCEV are most likely to be clustered. These include Berkeley, the South San Francisco Bay area, and southern Orange County.

Table 28: Public Hydrogen Refueling Stations Operating in California in October 2013

Station Name	Location	Commissioned
Burbank	145 W. Verdungo Ave. Burbank 91510	early 2011
Emeryville /AC Transit bus fueling & light duty	1172 45th St. Emeryville 94608	mid 2011
Fountain Valley	10844 Ellis Ave. Fountain Valley 92708	mid 2011
Newport Beach Shell	1600 Jamboree Blvd. Newport Beach 92660	mid 2011
Harbor City (Mebtahi/Chevron)	25800 S Western Ave. Harbor City (Long Beach) 90710	early 2011
Torrance Shell (ARB)	2051 W. 190th St. Torrance 90501	mid 2011
West LA Shell (Santa Monica 1)	11576 Santa Monica Blvd. Los Angeles 90025	mid 2008
Thousand Palms (U.S. DOE – Sunline Transit)	32505 Harry Oliver Trail Thousand Palms 92776	early 2000
UC Irvine	19172 Jamboree Blvd. Irvine 92616	early 2003

Source: CDFA/DMS staff

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[29] California Fuel Cell Partnership, *A California Road Map.*

2.2 Development of Hydrogen Fuel Dispenser Specifications and Standards

Project Objectives

As explained in Chapter 1, DMS has regulatory oversight of the fueling infrastructure and commercial sale of transportation fuels, including hydrogen, in California. BPC Section 12107 [30] requires DMS to adopt specifications and tolerances for dispensing equipment. Fuel dispensers for commercial hydrogen refueling stations must be evaluated by DMS to ensure they meet metrological specifications.

Specifications and test methods for transportation fuels and devices are developed by the National Conference on Weights and Measures (NCWM) and consensus standards-setting organizations, such as SAE International[31] (SAE). They are then published by NIST and NCWM in handbooks for use by weights and measures regulators. SAE International also promulgates standards. Since hydrogen is a new alternative fuel, many of the required specifications and standards did not exist at the start of this project. This situation presented a significant obstacle to the development of hydrogen infrastructure because of the legal requirements governing the retail sale of all transportation fuels.

To address this problem, the CEC contracted with DMS through Energy Commission Agreement 600-09-015 to develop the needed specifications, tolerances, and procedures, and to explore metrological standards for the required type testing of hydrogen dispensers. As part of this agreement, DMS was to accomplish the following tasks:

- Develop Specifications and Tolerances for the commercial measurement of hydrogen fuel delivery equipment for adoption by National Conference Weights Measures (NCWM).
- Develop type evaluation test procedures for the certification of dispensers and other measuring equipment used in commercial measurement.
- Research necessary test equipment to conduct type evaluation of Hydrogen Retail Motor Fuel Dispensers.
- Develop field test procedures for dispensers and other measuring equipment used in commercial hydrogen measurement.
- Develop method of sale requirements for dispensers for adoption by NCWM.
- Explore three types of reference standards that will be used to develop test procedures that can be used for type evaluation and field testing: gravimetric, volumetric and master meter standards.

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[30] The text of this regulation can be found in Appendix A.

[31] This organization was founded in 1905 as the Society of Automobile Engineers. In 1916, it changed its name to the Society of Automotive Engineers to emphasize its broad focus on all self-propelled (‘automotive’) vehicles. In 2006, the name changed again to SAE International.

- DMS will purchase the needed equipment and supplies to accomplish the goals stated above. DMS will release a competitive solicitation following the State Contracting Procedures to select and hire a test equipment fabrication company as a Subcontractor. In addition, DMS plans to retrofit existing space for equipment.

To accomplish the project objectives, DMS worked with NIST, NCWM, consensus standards organizations, fuel suppliers, manufacturers, and other stakeholders from across the hydrogen fuel industry.

The activities and outcomes for each of these tasks are discussed in the following sections of this report.

Development of Specifications, Procedures, and Model Codes for Hydrogen Dispensers

From the earliest stages of FCEV development, all stakeholders recognized that the uniform national standards and specifications were required, along with normalization with international standards. Although hydrogen has long been an industrial commodity around the globe, existing codes, standards, and practices do not cover the needs of the emerging market in hydrogen fuel. A set of uniform, fair, and appropriate metrological standards for hydrogen refueling equipment for use across the country was clearly necessary.

The U.S. DOE requested the NIST Office of Weights and Measures[32] to work with stakeholders on the development of such standards. In 2003, DOE asked the Office of Weights and Measures to evaluate metrological standards as they apply to hydrogen fuel and identify gaps. The Office of Weights and Measures received funding from DOE to promote development of metrology standards for hydrogen refueling equipment. DOE, along with the National Hydrogen Association and the U.S. Fuel Cell Council formed the National Hydrogen and Fuel Cell Codes and Standards Coordinating Committee. This committee, made up of a group of public and private stakeholders, was established to coordinate the development and implementation of hydrogen-related codes safety and standards for the hydrogen fuel industry.

To further this effort, the U.S. National Work Group (USNWG) for the Development of Hydrogen Measurement Standards was established under the sponsorship of NIST in October of 2007. The USNWG is comprised of a broad range of stakeholders. These include staff from DMS and NIST, other state regulatory officials, meter and dispenser manufacturers, industrial gas suppliers, standards and testing organizations, type evaluation laboratories, and other interested parties. DMS director Kristin Macey and DMS Measurement Standards Specialist III Robert (Norman) Ingram have played a leading role in the USNWG, contributing draft language and procedures, and providing review of final documents. Two subcommittees were established, one to develop equipment standards and test procedures, and one to develop fuel specification requirements. Director Macey serves as the Device Subcommittee Chairperson.

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[32] This office was previously called the Weights and Measures Division. The new name became official in October of 2011.

The goal of the USNWG was to develop a comprehensive set of model metrology standards for the commercial measurement of hydrogen fuel for vehicles and related applications. Specific areas addressed by the USNWG include:

- Device design, accuracy, installation, and use requirements.
- Method of sale requirements.
- Test procedures.
- Fuel quality standards.

The accomplishments of the USNWG to date include:

- The implementation of a tentative code in NIST *Handbook 44 Specifications, Tolerances, and Other Technical Requirements for Weighing and Measuring Devices.*
- Adoption of the method of sale requirement in NIST *Handbook 130 Uniform Laws and Regulations in the Areas of Legal Metrology and Engine Fuel Quality.*
- A checklist published in the NCWM National Type Evaluation Program (NTEP), *Publication 14©* to verify and document that hydrogen meters and dispensers meet the requirements of type evaluation and applicable regulations.
- Development of a draft examination procedures outline (EPO) for publication by NIST for field officials to use in routine regulatory compliance inspections of hydrogen fuel dispensers.

As provided in state law, these documents and procedures have been adopted into California's codes and regulations. Each of these items is discussed in more detail in the following sections.

NIST Handbook *44* Section 3.39 Hydrogen Gas-Measuring Devices – Tentative Code

One of the specific goals of the USNWG was the development of a comprehensive set of metrology standards for commercial hydrogen dispensers. These standards cover device design, accuracy, installation, use requirements, and tests procedures. Kristin Macey, Director of DMS, was the Device Subcommittee Chairperson leading this effort. The USNWG drew on the experience of its members from DMS and NIST with standards for compressed natural gas (CNG) motor fuel dispensing in drafting specifications and tolerances for hydrogen dispensers. Input was also received from industry representatives. In July 2010, the USNWG's draft code for hydrogen measuring devices was adopted by the National Conference on Weights and Measures. It was then published in the 2011 edition of NIST *Handbook 44* Section 3.39 as a 'tentative code'. Language included in Section 3.39 states that as tentative code: [it] "has only trial or experimental status and is not intended to be enforced. The requirements are designed for study prior to the development and adoption of a final code."[33] The code in Section 3.39 does not apply to wholesale deliveries of hydrogen fuel or to the sale of hydrogen where the amount dispensed does not affect the price to the customer (e.g., the current refueling model for leased FCEVs in California). Subsection N. prescribes the procedures to be followed for testing of retail hydrogen dispensers.

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[33] NIST *Handbook 44 Specifications, Tolerances, and Other Technical Requirements for Weighing and Measuring Devices* 2013. Section 3.39.

The latest edition of NIST *Handbook 44* is automatically adopted by reference in California, along with any deletions and additions that have been approved through the state's rulemaking process. Accordingly, the tentative code in *Handbook 44* Section 3.39 is included in the CCR, Title 4, Division 9, Chapter 1, Article 1.

The requirements that DMS adopts from *Handbook 44* are intended to prevent inaccurate quantities being delivered by commercial weighing and measuring devices. All mechanical devices have some error in their indications, so for each class of device, an accuracy tolerance is established. The accuracy tolerance is the acceptable error in the indicated delivery of a device. The accuracy tolerance must be small enough that neither the buyer nor the seller suffers economic harm in a transaction.

Two types of accuracy tolerances are established for weighing and measuring devices. The acceptance tolerance applies during type evaluation and initial testing after installation or repair. The acceptance tolerance is typically smaller than the maintenance tolerance, which is applied during routine testing after the device has been in service for more than 30 days.

Subsection T.2 in Section 3.39 sets an acceptance tolerance of 1.5 percent and a maintenance tolerance of 2.0 percent on the indicated delivery of the hydrogen fuel measuring devices. After Section 3.39 was accepted by the USNWG, some industry representatives expressed a concern that these tolerances were too restrictive given the unique properties of hydrogen gas and the cost needed to design and build high-accuracy devices. In their view, the limited market for hydrogen dispensers did not justify the capital investment needed to achieve the tolerances in Section 3.39.

In November 2013, DMS posted its proposed deletions and additions to Section 3.39 of the CCR for the required public comment period. The most significant of the proposed modifications was a temporary relaxation of the accuracy tolerances specified in Subsection T2. In February 2014, the rulemaking package was submitted to the Office of Administrative Law. Final approval was obtained from the Office of Administrative Law and the regulation became effective on June 16, 2014, making Section 3.39 enforceable in California. These changes are to the CCR only, not NIST *Handbook 44*, and therefore will be effective only in California. The most recent version of Section 3.39 is located in Appendix F, but the proposed deletions and additions are not reflected in that version.

The regulation establishes three additional accuracy classes, as shown in Table 29. The underlined entries in Table 29 are proposed additions to the tentative code. Dispensers in Accuracy Class 10.0 will be accepted if installed in California before the end of 2017; after this date all new hydrogen dispensers must meet the tolerances in Accuracy Class 5.0 or better. New dispensers installed after January 1, 2020 must meet Accuracy Class 2.0. It is expected that improvements in technology will enable all new dispensers to meet the requirements of Accuracy Class 2.0 by 2020.

Table 29: Proposed Accuracy Classes and Tolerances for Hydrogen Gas-Measuring Devices in California

Accuracy Class	Application or Commodity Being Measured	Acceptance Tolerance	Maintenance Tolerance
2.0	Hydrogen gas as a vehicle fuel	1.5 %	2.0 %
3.0 [1]	Hydrogen gas as a vehicle fuel	2.0 %	3.0 %
5.0 [1]	Hydrogen gas as a vehicle fuel	4.0 %	5.0 %
10.0 [2]	Hydrogen gas as a vehicle fuel	5.0 %	10.0 %

[1] The tolerance values for Accuracy Classes 3.0 and 5.0 hydrogen gas-measuring devices are applicable to devices installed prior to January 1, 2020.

[2] The tolerance values for Accuracy Class 10.0 hydrogen gas-measuring devices are applicable to devices installed prior to January 1, 2018.

Source: CDFA/DMS staff

NIST *Handbook 130 -* Adoption of Method of Sale Requirements for Hydrogen Dispensers

The method of sale of a commodity refers to the number, volume, or weight for which a unit price is set. Establishing a uniform method of sale for a commodity ensures that sellers advertise and deliver a product using a single unit of measurement. This enables consumers to make value comparisons quickly and simply.

In October 2007, the USNWG recommended the kilogram unit of mass as the retail method of sale for hydrogen. One kilogram of hydrogen has an energy value comparable to that of a gallon of gasoline. As a result, the kilogram is an acceptable method of sale from both a metrological and consumer standpoint.

The USNWG recommendation also included a definition for "hydrogen fuel" developed by DMS, which reads, "A fuel composed of molecular hydrogen intended for consumption in a surface vehicle or electricity production device with an internal combustion engine or fuel cell."[34]

In 2010, regulations governing the method of sale of hydrogen fuel and the DMS definition of "hydrogen fuel" were added to NIST *Handbook 130 (Handbook 130 –* 2013 2.32 Retail Sale of Hydrogen Fuel (H)). The complete text of these regulations is given in Appendix F.

The method of sale requirements for transportation fuels also specify dispenser labeling and signage at retail outlets. *Handbook 130* specifies that the unit price of hydrogen fuel be expressed in whole cents per kilogram. Both hydrogen dispensers and signage and retail stations must be labeled with the unit price and the delivery pressure in units of bars or MPa.

NCWM *Publication 14©* Checklist for the Type Evaluation of Retail Hydrogen Dispensers

The NCWM administers the NTEP. All commercial weighing and measuring devices must undergo type evaluation to show they conform to NIST *Handbook 44* requirements. Type

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[34] NIST *Handbook 130 Uniform Laws and Regulations in the areas of legal metrology and engine fuel quality 2014edition* Section 2.32.1, page 133.

evaluations are conducted by officials from laboratories participating in NTEP[35]. Devices that meet *Handbook 44* requirements receive Certificates of Conformance and are then legal for use in commerce in the forty-six states that require NTEP Certificates[36]. The NCWM publishes checklists to assist weights and measures officials when conducting type evaluations. These are published in NCWM *Publication 14© Technical Policy, Checklists and Test Procedures*[37].

Within California, DMS oversees a parallel program, the California Type Evaluation Program. DMS is also an active participating laboratory in NTEP and is a member of National Type Evaluation Technical Committees formed to develop or revise type evaluation checklists. These technical committees also work to maintain consistency between NTEP checklists and *Handbook 44* requirements.

BPC Section 12500.5 requires that all commercial weighing and measuring devices be approved before they can be sold and installed in California. Section 12500.8 authorizes the California Type Evaluation Program to recognize NTEP Certificates of Conformance. Generally, DMS uses the checklists of *Publication 14©* for type evaluation of devices in California. However, the California Type Evaluation Program develops and uses its own type evaluation checklists if a device type is not covered in *Handbook 44* (e.g., watt-hour meters).

At the start of this project, there was no official type evaluation checklist for hydrogen dispensers, either in California or nationally. DMS had developed a draft checklist for hydrogen dispensers in 2008; however, the adoption of NIST *Handbook 44* Section 3.39 was required before a code-specific checklist could be written for *Publication 14©*.

In 2010, the National Type Evaluation Technical Committee – Measuring Sector established a subcommittee made up of DMS staff members Robert (Norman) Ingram, Dan Reiswig, and Van Thompson to update and complete the draft DMS checklist for national use. The USNWG also reviewed the checklist during its meetings in September and October 2010. At its annual meeting in 2011, the National Type Evaluation Technical Committee - Measuring Sector unanimously agreed to send a proposal to the NCWM NTEP Committee to include the new checklist in *Publication 14©*. The recommendation was approved the NCWM NTEP Committee at its January 2012 meeting and the checklist was included in the 2012 Edition of *Publication 14©*.[38]

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[35] Besides DMS, the following are participating laboratories in NTEP: Grain Inspection Packers and Stockyard Administration (GIPSA), Washington, D.C.; Maryland Department of Agriculture, **Annapolis,** MD; NIST Force Group, Gaithersburg, MD**;** New York State Bureau of Weights & Measures, Albany, NY; North Carolina Department of Agriculture , Raleigh, NC; Ohio Department of Agriculture, Reynoldsburg, OH; and Measurement Canada, Ottawa, Canada.

[36] As of 2010, North Dakota, Rhode Island, Texas, Vermont, and the Virgin Islands do not require an NTEP certificate before a weights and measures device is placed in service. Map of NTEP certificates: http://www.scalemanufacturers.org/PDF/NTEPmaps.pdf, accessed Jan 10, 2020.

[37] NCWM *Publication 14©* is protected under copyright laws, and excerpts may not be reproduced in this report. Purchase NCWM publications online: http://www.ncwm.net/publications, accessed Jan 10, 2020.

[38] NCWM 2012 Annual Meeting Archives

Field Test Procedures – *EPO No. 29*

An Examination Procedure Outline (EPO) is followed by weights and measures officials to conduct routine inspection of a device and may be used as a reference in a type evaluation. Since hydrogen fuel dispensers represented a new device class in *Handbook 44*, a new EPO had to be developed for use in type evaluation and field testing.

The Weights and Measures Division of NIST drafted *Examination Procedure Outline (EPO) No. 29 for Hydrogen Gas (H*$_2$ *Gas) Retail Vehicle Fuel Dispensers (EPO No. 29)* with guidance from the USNWG. *EPO 29* includes inspection and field test procedures, with code references to NIST *Handbook 44*. The draft of *EPO 29* was sent to government and industry stakeholders for comment and evaluation. When its review is completed, *EPO 29* will be accepted by NIST for future publication. A draft version of *EPO No. 29* is now available to weights and measures officials for type evaluation and testing of hydrogen dispensers.

DMS will publish the hydrogen device EPO as a policy document when the hydrogen device regulations become effective. This means that California weights and measures officials will soon be able to use this EPO for enforcement purposes.

Design and Development of Working Standards for Type Evaluation and Field Testing of Dispensers

Prior to this project, much of the existing data on high-pressure hydrogen dispensing equipment was the property of dispenser and flow meter manufacturers. To develop and enforce the codes and regulations necessary for the retail sale of hydrogen fuel, DMS needed verifiable information on dispenser performance, as well as equipment to certify hydrogen dispensers. In order to test the accuracy of hydrogen dispensers, a physical reference standard was necessary; however, no recognized physical standards had been yet identified. The final component of the hydrogen dispenser project called for DMS staff to explore three types of working standards that might be suitable for type evaluations and field testing of hydrogen dispensers.

As used here, the term working standard refers to a physical apparatus used to evaluate, verify, and test the performance of a commercial device. Under this project, three types of working standards were investigated:

- Gravimetric Standard: Hydrogen gas is dispensed into tanks similar to those installed in fuel cell vehicles. The tanks are weighed on a scale before and after filling. The difference between the two measurements is the mass of hydrogen dispensed
- Volumetric or Pressure-Volume-Temperature (PVT) Standard: Hydrogen gas is dispensed into tanks similar to those installed in fuel cell vehicles. The density of the gas in the tank is calculated from pressure and temperature measurements on the gas using the NIST equation of state values. By multiplying the density by the tank's known internal volume, the mass of hydrogen dispensed into the field reference standard can be calculated
- Master Meter Standard: A master meter standard is a direct one-to-one comparison of the readings of a standard and a test device. For testing hydrogen dispensers, a flow meter that has been thoroughly characterized in a calibration laboratory is placed between the dispenser and the vehicle tank. After the tank is filled, the total flow from this master meter is compared to the dispenser reading

DMS did not have resources or equipment for the design or fabrication of standards. As called for under the contract with the CEC, a request for proposal was issued through the California Department of General Services to solicit competitive bids for fabrication of the standards. The contract was awarded to the NREL in Golden, Colorado.

After the contract was signed in February 2012, DMS and NREL representatives met to review the scope of work and detailed plans to establish requirements and criteria for the physical standards to be fabricated. NREL proposed incorporating all three standards into one package, the Hydrogen Field Standard (HFS). The DMS/NREL agreement called for test trials at hydrogen dispensing stations throughout California. The purpose of these tests was to validate standards and compare the uncertainties of the three standards in the HFS. As explained below, it was later agreed that validation testing should be conducted at NREL's facility, where the required controlled conditions could be maintained.

Design Considerations for Hydrogen Fill Tanks and Dispensers

CNG is an established gaseous alternative transportation fuel. Like CNG, hydrogen fuel is stored and dispensed as a high-pressure gas. Consequently, there are many similarities between the storage and delivery systems for hydrogen and CNG. Many of the hydrogen codes and regulations were modeled on the corresponding language for CNG. However, the unique properties of hydrogen call for special considerations in the design and fabrication of storage tanks and dispensers.

The maximum pressure of CNG fuel systems is typically 3,600 psi or less. Because of the lower energy density by volume of hydrogen, hydrogen fuel systems must operate at much higher pressures, either 5,000 psi (35 MPa) or, more commonly today, 10,000 psi (70 MPa). At these pressures, vehicles can store enough fuel on board for an acceptable driving range of at least 300 miles. Bulk storage tanks at hydrogen stations are pressurized to 13,000 psi so that they can deliver the required fill pressures.

Because of its extremely small size, a molecule of hydrogen can diffuse through many materials, both metallic and non-metallic. This property is a challenge in the design of storage containers for hydrogen. The molecular bond in hydrogen can be broken at the surface of many metals, releasing free hydrogen atoms. These atoms can rapidly diffuse into the bulk metal where they produce defects that can lead to fracturing in a process known as hydrogen embrittlement. All materials and components in contact with hydrogen must be specifically rated for hydrogen service. The use of incompatible materials will cause excessive leakage and may lead to a failure of component or storage vessel.

The dispenser nozzle provides an electronic interface for communication between the vehicle and dispenser controllers and a secure grounding connection. During refueling, the internal temperature of the storage tanks rises as the hydrogen is compressed. These tanks have a maximum temperature rating, so the rate of fill must be controlled to prevent overheating. When a FCEV is refueled, sensor data from the vehicle storage tanks is transmitted through the nozzle interface so that the dispenser will automatically shut off if an unsafe condition develops.

The HFS is equipped with a standard receptacle that accepts a hydrogen dispenser nozzle. However, the HFS does not have an electronic communications interface. The tanks in the HFS have temperature sensors that are continuously monitored by the system controller. If a temperature set point is exceeded, the controller will automatically abort the test in progress.

HFS – Description and Specifications

Critical design requirements for the HFS included an apparatus that is transportable by an available vehicle, such as an industrial van or truck, and with no special power requirements (e.g., standard 125 VAC or battery-power). A purge system provides a controlled release of hydrogen following a fill test from the pressurized tanks. Certified weights covering the range of the balance are used to provide in-field validation of the balance accuracy.

The major components of the HFS are:

- The three working standards (gravimetric, volumetric, and master meter).
- A programmable logic controller.
- Data acquisition and display electronics.
- Two hydrogen fill tanks.
- Piping and valves connecting the tanks, standards, and hydrogen source.
- A supporting framework for mounting and transport.

The HFS has two storage tanks connected in parallel, each with a capacity of 2 kg. Since the HFS was designed for transport on a van or truck, commercial hydrogen-compatible Composite Overwrap Pressure Vessels constructed with carbon fiber tape were specified to reduce the weight of the apparatus. Tanks of this construction are also used in FCEVs to minimize weight. Each fill tank is fitted with a certified high-pressure transducer and three certified temperature sensors to track and record internal conditions of the tank.

The original contract between DMS and NREL specified one 2 kg and one 4 kg storage tank for the HFS. Composite Overwrap Pressure Vessel tanks are manufactured in limited quantities and are used in many applications, including the storage of CNG. The tanks needed for the HFS were in short supply across the country when the components of the HFS were ordered and no 4 kg Composite Overwrap Pressure Vessel tanks were available. Consequently, two different types of 2 kg tanks were accepted for the HFS.

Figure 28 shows the front view of the assembled HFS. Hydrogen Fill Tank 1 can be seen on the left and Fill Tank 2 on the right. Hydrogen fuel dispensers operate at 5000 and 10,000 psi (35 and 70 MPa) and both fill tanks are certified for operation at 10,000 psi (70 MPa).

Fill Tank 1 is a Type III high-pressure storage cylinder as defined by ANSI/AGA Standard NGV2-2000.[39] It was manufactured by Dynetek Industries[40], weighs 54.55 kg and has a water volume[41] of 57.9 L at zero pressure. It consists of an aluminum liner wrapped in carbon fiber composite tape. Fill Tank 2 was manufactured by Lincoln Composites, Inc. It is a Type IV storage cylinder weighing 54.55 kg with a water volume of 65.0 L at zero pressure. Tank 2 has

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[39] The fill tanks conform to ANSI/AGA Standard NGV2-2000, developed for on-board storage for compressed natural gas vehicles. A discussion of safety standards and specifications for on-board storage tanks can be found at *An Overview of NGV Cylinder Safety Standards, Production and In-Service Requirements*, Mark Trudgeon, July 2005.

[40] A complete Parts and Identification list for the HFS can be found in Appendix G.

[41] The effective working volume of a vessel is determined by filling it with water. From the weight of the water, and knowing the temperature and pressure inside the vessel, its volume may be determined from tables of water density.

a polymeric liner that is wrapped in carbon fiber composite tape. Tank 2 has a larger diameter and shorter length than Tank 1. The relative diameters of the tanks can be seen in Figure 29.

Figure 28: DMS Hydrogen Field Standard (HFS)

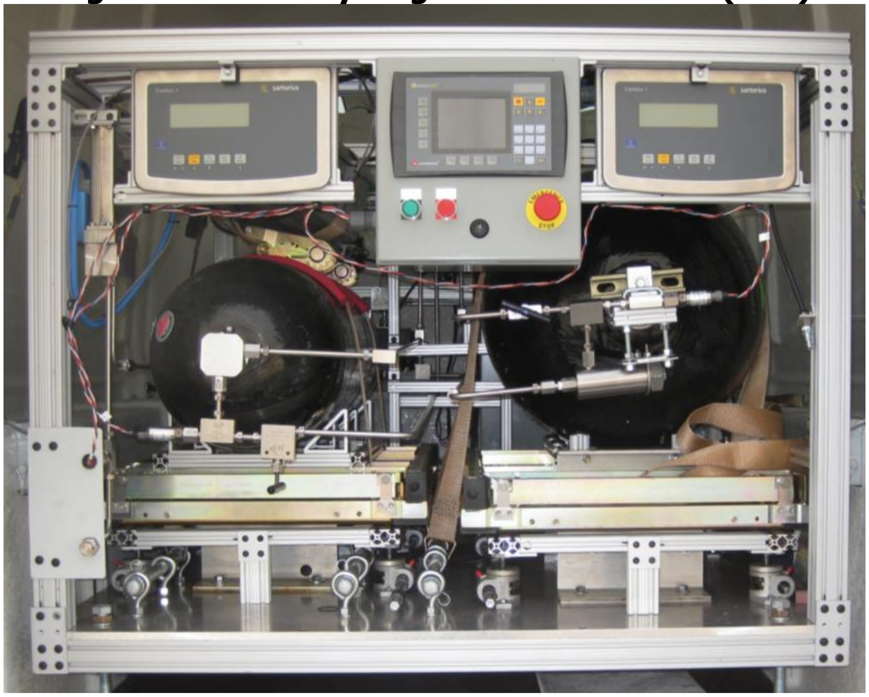


Photo Credit: DMS Hydrogen Laboratory

The first step in the construction of the HFS was the adaptation of the fill tanks to accommodate the necessary temperature and pressure sensors. Interface hardware was developed and installed by NREL. Each tank is equipped with an internal pressure transducer and three internal temperature transducers that continuously monitor the conditions during testing.

Figure 29: View of DMS HFS Fill Tanks

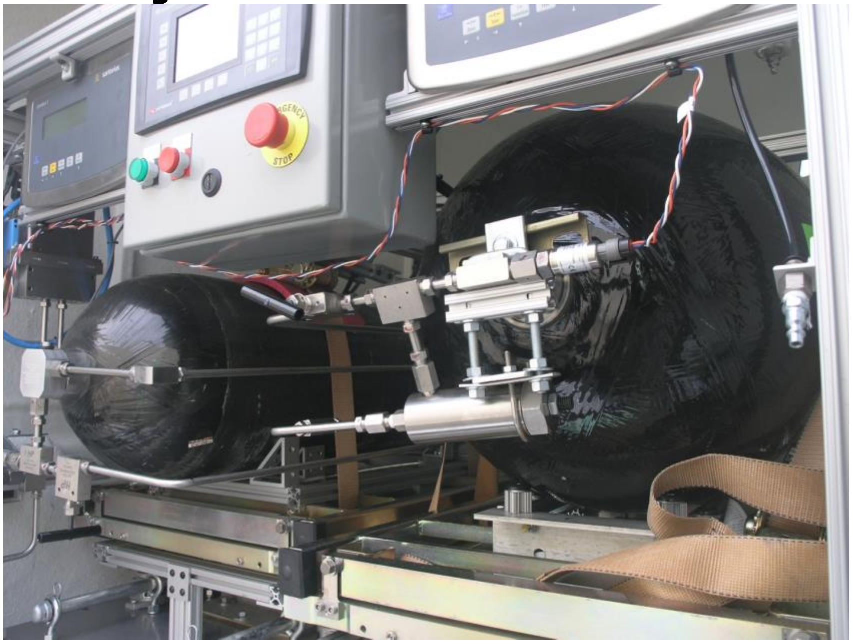


Photo Credit: DMS Hydrogen Laboratory

The displays for the scales are located on either side of the master display/control unit seen in the top center of the photograph. The components of the Data Acquisition Control System are mounted within the framework behind the storage tanks. The Data Acquisition Control System monitors all detectors during a fill test. The programmable logic controller is programmed to control critical protocols during data acquisition and analysis. The Data Acquisition Control System is based on LabVIEW, a proprietary software system for instrument control, data acquisition, and analysis. LabVIEW is a product of National Instruments Corporation. The main functions of the Data Acquisition Control System are to monitor and record sensor readings, including pressure, temperature, and safety sensors.

Fill parameters (temperature, pressure, and cylinder volume) are also monitored in real time. Algorithms relating fill parameters (e.g., fill time, and mass flow rate) were developed by NREL staff to provide accurate, real-time indications of dispensed hydrogen.

Pneumatic valves control both the filling of the tanks and the controlled emptying of the tank following a test. Critical safety features, including pressure relief devices and other elements (bypass and other release systems) were built into the tank pneumatic system. Automatic emergency protocols are designed to safely halt a test in the event of an out-of-range condition (e.g., excessive pressure or temperature). The system includes many safety features, including Pressure Relief Devices for emergency depressurization, and control systems for user-initiated purging of pressurized cylinders.

Gravimetric Working Standard - Description

The Gravimetric Working Standard uses two precision temperature-compensated, calibrated platform scales to measure the change in the weight of its two tanks during a hydrogen fill. The scales have a resolution of one gram. The high resolution of the scales ensures that their contribution to the uncertainty of the measurement of the mass of hydrogen dispensed is negligible. Thus, errors in the scale readings will be negligible compared to other uncertainties in the measurement. The mounting of the storage tanks on the scales was designed to isolate the dispensing interface so that it does not contribute to the determination of the weight of hydrogen dispensed. The accuracy of the scales was validated at the NREL metrology laboratory using NIST traceable standards.

Master Meter Working Standard - Description

The Master meter standard uses a Coriolis meter that measures the displacement of flow tubes as hydrogen passes through.

Volumetric Working Standard - Description

The Volumetric Working Standard uses data from the internal temperature and pressure transducers in the storage tanks along with the previously determined tank volumes to determine the mass of hydrogen dispensed during a fill.

Algorithms to convert the sensor and empirical parameters (pressure, temperature and cylinder volume) to hydrogen mass were developed. Multiple internal temperature sensors were installed to track temporal temperature gradients. Temporal monitoring of internal temperature facilitates recognition of thermal steady-state conditions. This was confirmed in the on-site testing. Analysis for delivered hydrogen is based on the NIST equation of state data for hydrogen already in use within NREL’s hydrogen and fuel cell technologies program. Corrections for pressure-induced changes in cylinder volume were developed. Prior to use, sensor and transducer accuracy is validated using NIST traceable methods at the NREL metrology laboratory.

HFS Testing and Generation of Control Chart Data at NREL

Following full system integration, the HFS was extensively tested on site at NREL using the existing Wind-to-Hydrogen production, storage, and dispensing capabilities. A final safety review of the HFS and operating protocols was held prior to system testing. Since the HFS was designed for permanent installation in a vehicle, the system was mounted on similar supports for the testing at NREL. The HFS was designed to operate in wind conditions of up to 20-30 mph. To assess the impact of wind on stability and accuracy of the HFS, environmental data, including wind speed and ambient temperature, barometric pressure, and relative humidity were recorded during testing.

Originally, it was planned that system validation and the generation of control chart data would be conducted as part of field testing by DMS in California. However, in the course of the testing at NREL, it was recognized that the validation process demanded precisely controlled quantity and flow conditions that could not be maintained in the field. In addition, the generation of control chart data would interfere with the operation of a retail station and would require significant quantities of hydrogen that could not be recovered. Accordingly, the agreement between DMS and NREL was modified to allow the validation and control chart data to be generated at NREL. A high volume stationary 70 MPa storage tank had to be installed at NREL so that high pressure testing could be performed.

One of the goals of this research project was to develop a working standard for determining the delivery in kilograms of a hydrogen dispenser. As used here, the word ‘standard’ means a physical device used to test a weighing or measuring device. Three different standards - gravimetric, master meter, and PVT - were evaluated to determine their suitability for use as a working standard.

For this application, the gravimetric method was the only procedure that could be directly traced to the kilogram reference standard. Therefore, the standard mass used to verify the gravimetric working standard was also used as a reference for the master meter and PVT working standards to establish control charts.

The validation work was delayed when the first tank ordered failed to meet quality specifications during testing at the fabricator.

Generation of Control Charts

Control charts were generated with two objectives: first, to demonstrate attainment of statistical control of the measurement process of the HFS and second, to evaluate the pressure-volume-temperature and master meter standards relative to the known gravimetric measurement incorporated in the HFS. A detailed guide to control charts and the associated statistics may be found in *NIST/SEMATECH e-Handbook of Statistical Methods,* October 2013 (http://www.itl.nist.gov/div898/handbook/).

A minimum of 7 – 12 independent measurements are required to establish an initial control chart. No two data points can be determined on the same day. Replicate tests made on the same day estimated the short-term standard deviation and may not indicate the actual variability of the process. A control chart with 25 to 30 independent data points is required to make statistically valid decisions and to calculate uncertainties.

For this project, the three standards were tested with drafts of 2 kg at 35 MPa and 4 kg at 70 MPa. Section 3.2 *Tolerances of Standards* in NIST *Handbook 44 Appendix A* recommends that the accuracy of standards used in testing commercial weights and measures devices be no more than one-third the applicable device tolerance if the standard is used without a correction. The acceptance tolerance for hydrogen dispensers established in Section 3.39 is ±1.5 percent of the indicated quantity, or 0.030 kg (30 g) and 0.060 kg (60 g) for the 2 kg and 4 kg drafts, respectively. Therefore, after applying a factor of one-third, the combined error plus the uncertainty for each standard must be less than 10 g for the 2 kg drafts, and 20 g for the 4 kg drafts.

To minimize both the amount of hydrogen and the time required for validation, the test plan evaluated the three standards simultaneously. The gravimetric method used two temperature-compensated balances with a resolution of 1 g. For the volumetric method, the computer program NIST Standard Reference Database 23 "NIST Reference Fluid Thermodynamic and Transport Properties Database: Version 8.0 was used to determine the volume. Finally, a temperature-compensated master meter was read directly by the HFS control module.

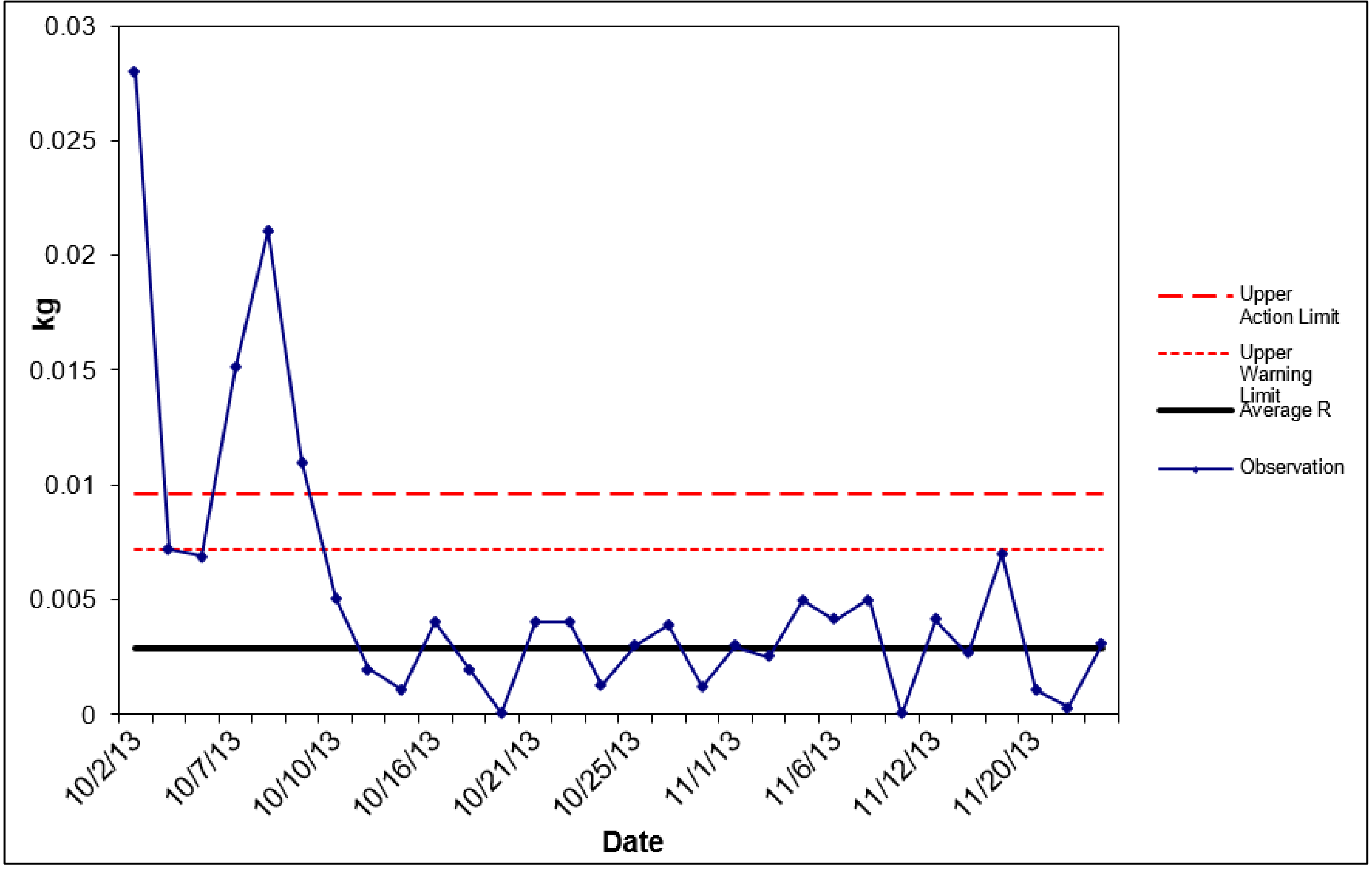
Range (R) charts with a subgroup size of n=2 were developed for each of the three standards for the 2 kg drafts taken at 35 MPa and the 4 kg drafts taken at 70 MPa. R charts were developed. S charts were not used, because the subgroup size was less than eleven. R charts evaluated the uncertainty associated with the measurement process of replicate tests. For a detailed explanation of R and S charts, see Section 6.3.2.1 in *NIST/SEMATECH e-Handbook of Statistical Methods* at http://www.itl.nist.gov/div898/handbook/pmc/section3/pmc321.htm.

Two replicate tests were made each day. Table 30 shows representative data collected on Day 15 of the collection process. Data was collected at approximately 200 individual time points for each replicate. Table 30 includes readings spaced throughout the first test of Day 15. The absolute differences between each day's replicate tests were used to calculate the range with one degree of freedom per replicate test. The range was divided by the square root of 2 (n=2) to give an estimate of the standard deviation of the normal distribution.

Control charts were constructed by plotting the average of the range, observed values for each day, upper warning limit, and upper control limit. With a sub-grouping of n=2, the lower control limit and lower warning limit are equal to zero. The upper warning limit is calculated by multiplying the average of the range by 2.512 and the upper control limit by 3.267. These limits are critical values of the t-test parameter for confidence intervals of 95 percent and 99.7 percent based on a sample size of 30 (values from NIST Technical Note 1297). Observations plotted on the control chart falling outside the upper control limit would indicate a decrease in precision leading to possible problems with the standard or process.

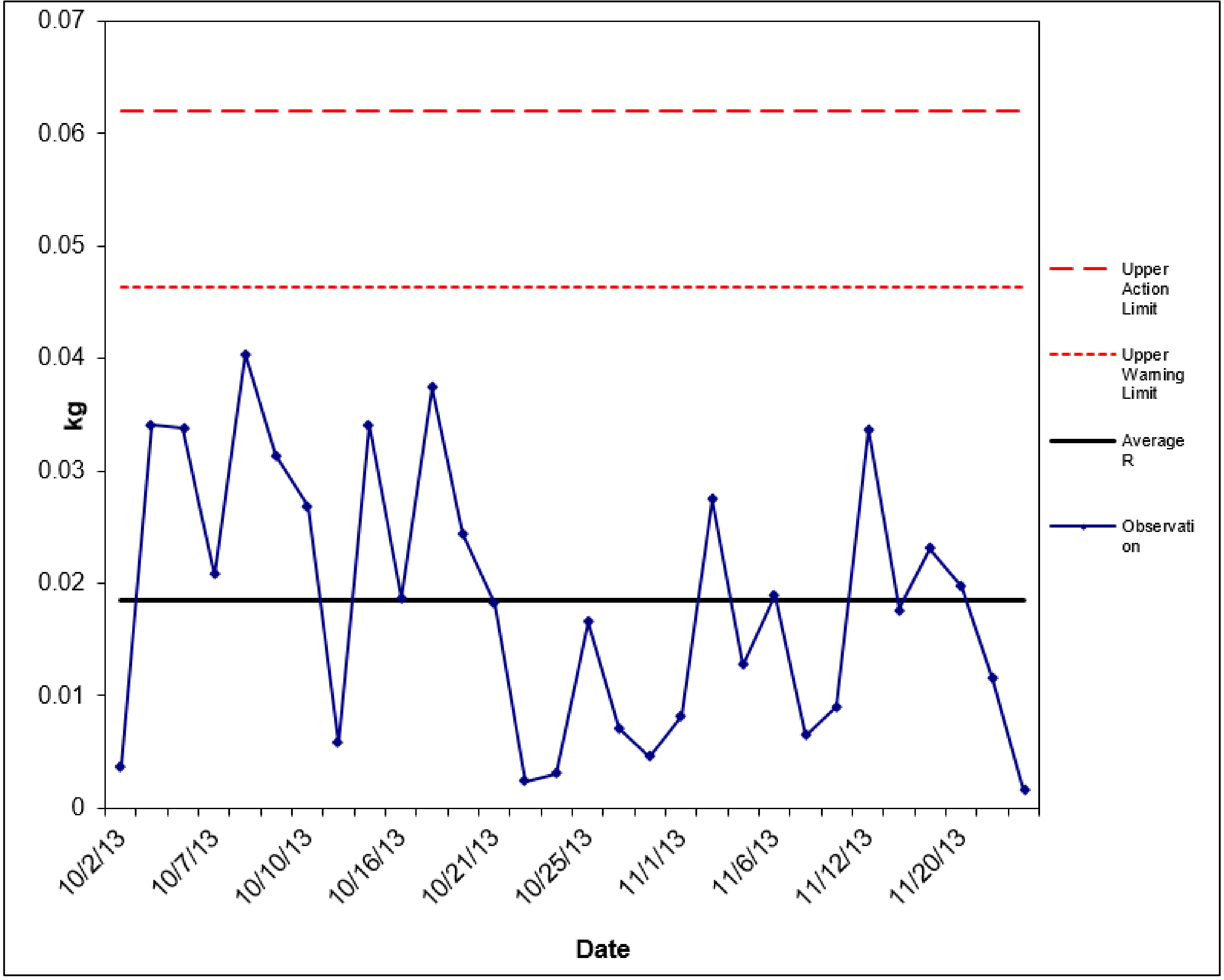
The control charts for each of the standards at 35 and 70 MPa are shown in Figures 30-35.

Figure 30: Gravimetric Standard Control Chart (35 MPa)



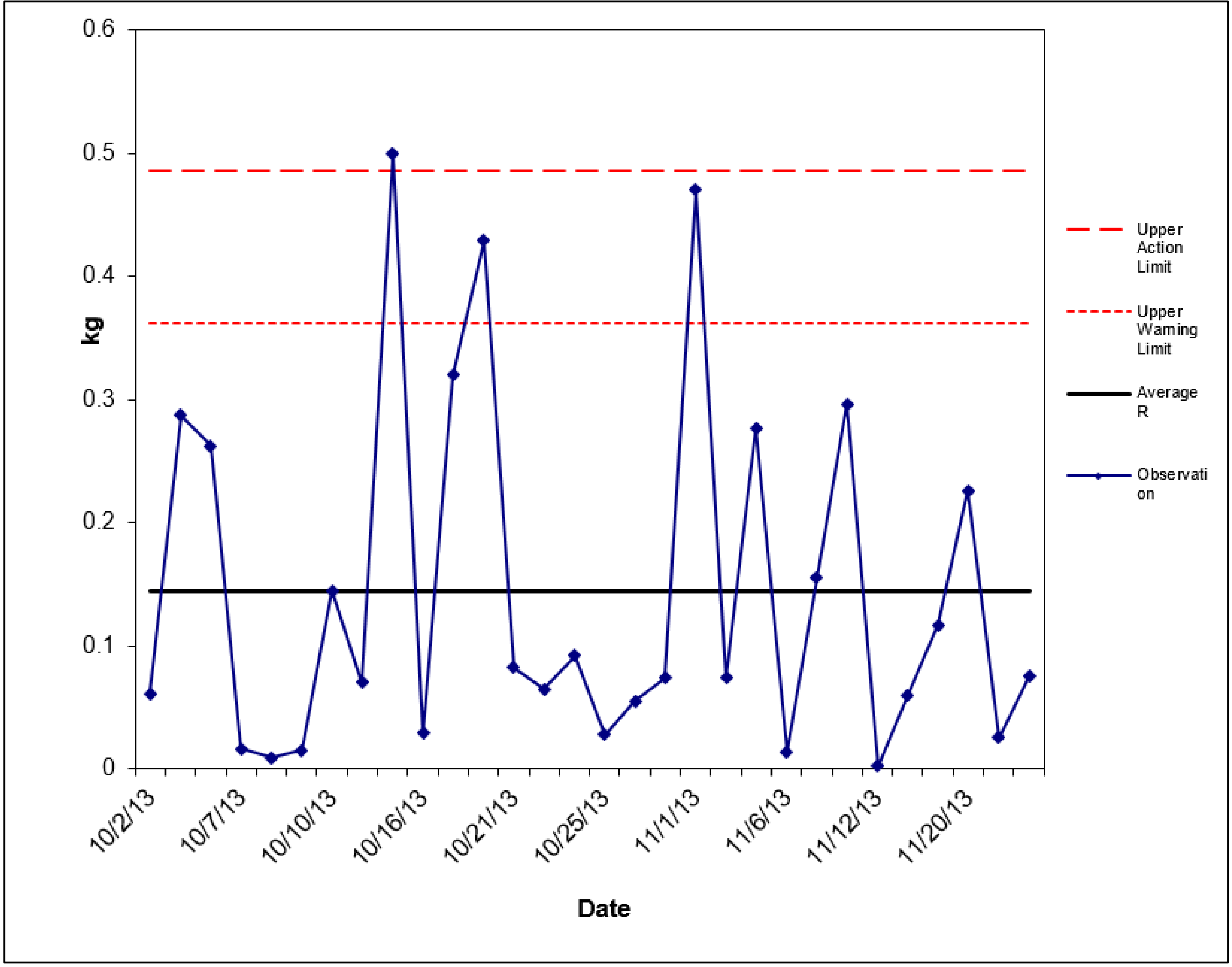
Source: CDFA/DMS Metrology Laboratory

Figure 31: PVT Standard Control Chart (35 MPa)



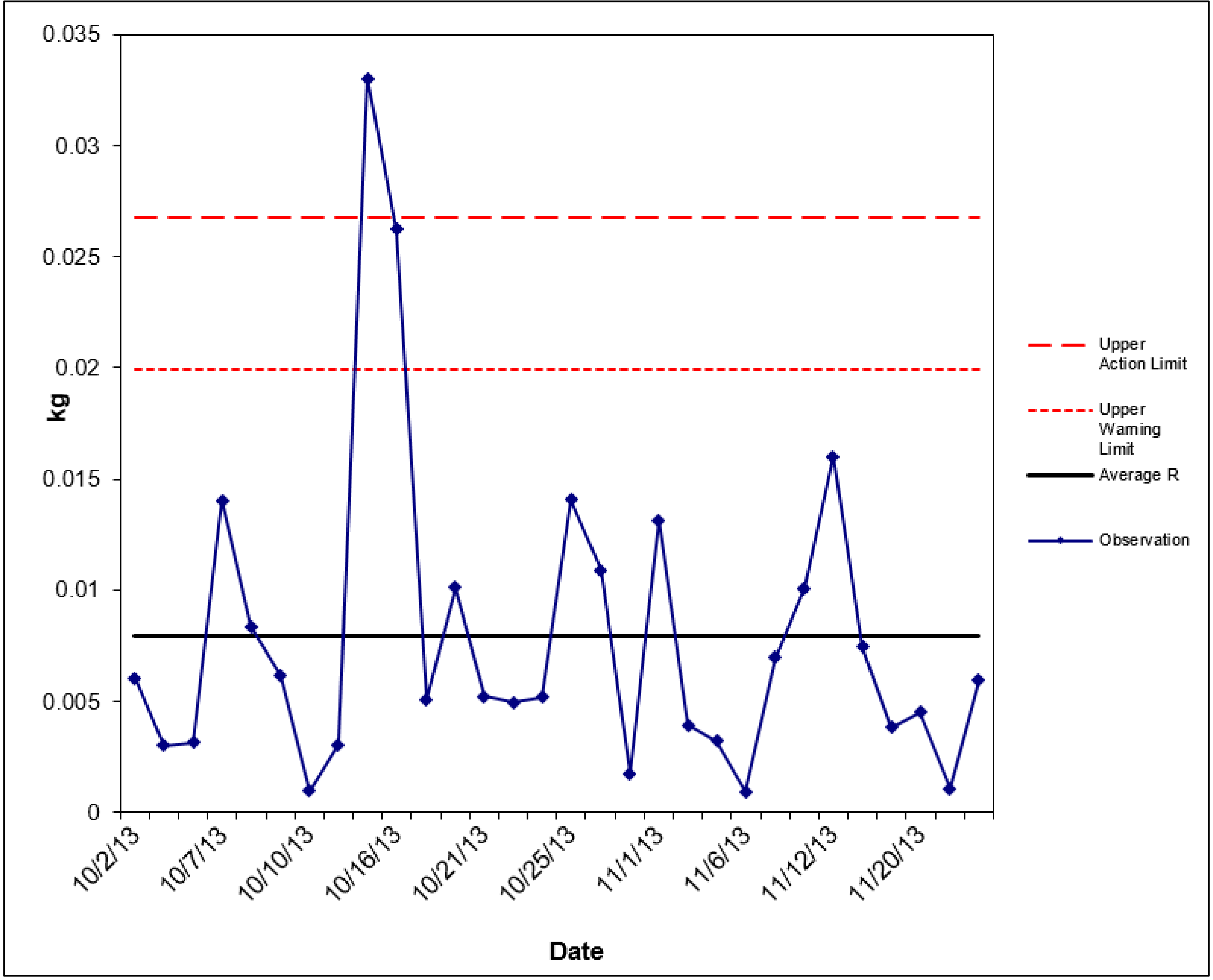
Source: CDFA/DMS Metrology Laboratory

Figure 32: Master Meter Control Chart (35 MPa)



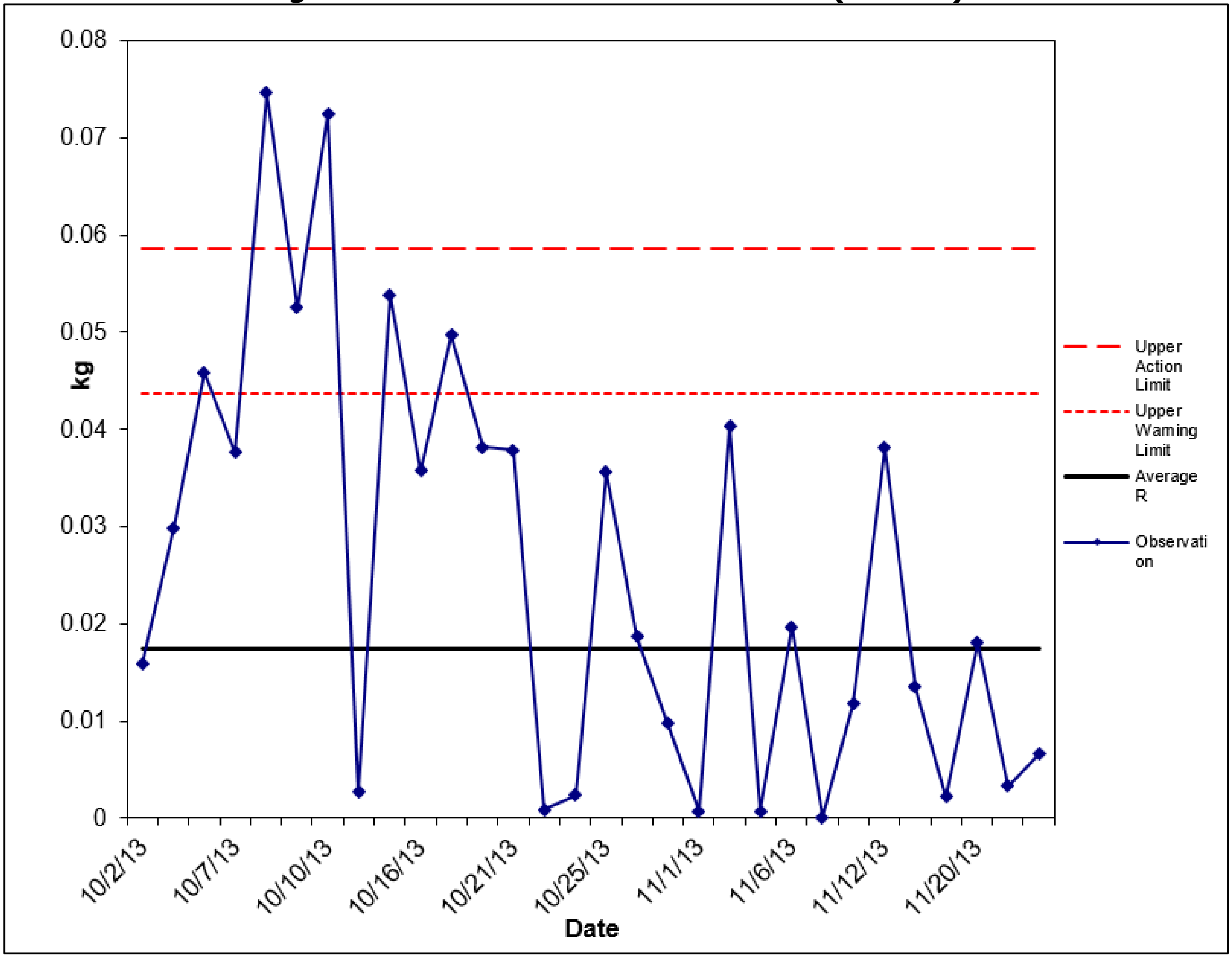
Source: CDFA/DMS Metrology Laboratory

Figure 33: Gravimetric Standard Control Chart (70 MPa)



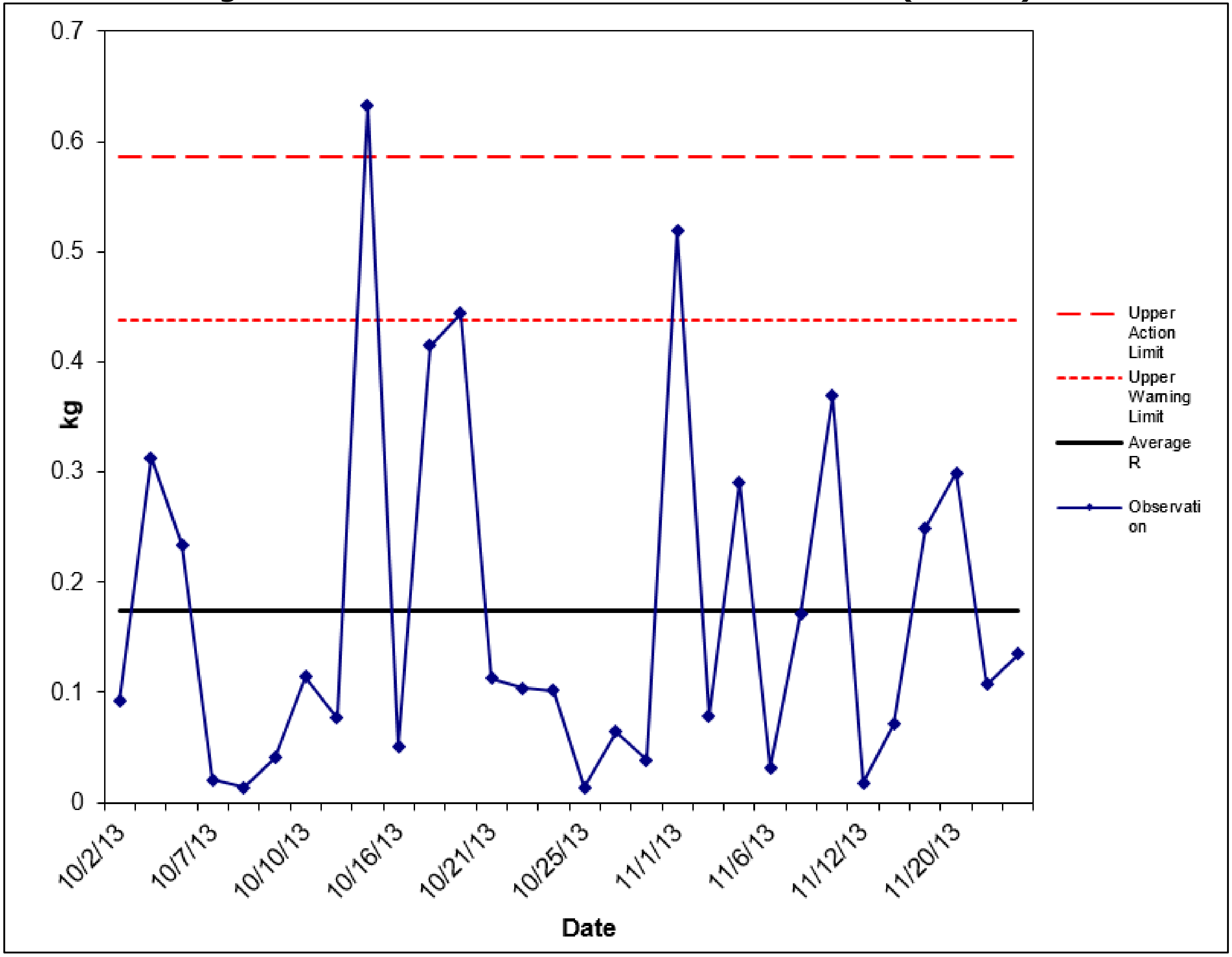
Source: CDFA/DMS Metrology Laboratory

Figure 34: PVT Standard Control Chart (70 MPa)



Source: CDFA/DMS Metrology Laboratory

Figure 35: Master Meter Standard Control Chart (70 MPa)



Source: CDFA/DMS Metrology Laboratory

Table 30: Selected Fill Data from Day 15 (10/23/2013)

Reading	2	13	24	35	46	58	69	80	101	112	124	135	146	158	169	180	191	198
Time (Min.)	1154	1157	1201	1205	1210	1231	1235	1240	1247	1616	1620	1624	1629	1709	1714	1717	1747	1748
Time (Sec.)	53	41	58	17	6	51	58	17	48	13	44	46	48	38	51	46	37	13
Tank1 Temp0 (deg C)	16.2	41.5	42.5	46.5	41.2	34.4	52.3	60.1	57.2	38.8	38.3	44.5	40.2	39.5	48.3	59.3	48.1	48.0
Tank1 Temp1 (deg C)	16.5	41.5	42.4	47.3	41.8	35.0	51.8	60.3	57.8	39.0	39.3	45.4	40.7	39.8	48.0	59.9	48.4	48.3
Tank1 Temp2 (deg C)	16.9	43.0	43.3	48.3	42.3	35.2	52.5	61.0	58.4	40.8	40.1	46.3	41.2	40.1	48.4	60.1	48.8	48.6
Tank1 Temp Avg (deg C)	16.5	42.0	42.7	47.3	41.7	34.8	52.2	60.4	57.8	39.5	39.2	45.4	40.7	39.8	48.2	59.7	48.4	48.3
Tank1 Pressure (psig)	153.1	1386.0	2714.8	4018.1	3967.3	3919.5	5741.4	7876.9	9609.6	1017.3	2479.8	3873.6	3936.0	4603.1	6223.2	8711.5	9326.7	9321.8
Tank1 Mass PVT (kg)	0.055	0.407	0.755	1.052	1.057	1.067	1.399	1.761	2.055	0.306	0.703	1.025	1.053	1.205	1.508	1.903	2.054	2.054
Tank1 Weight Scale (kg)	0.000	0.355	0.699	0.999	2.006	1.002	1.344	1.703	2.004	0.253	0.657	0.977	1.004	1.149	1.451	1.853	3.006	2.006
Tank2 Temp0 (deg C)	15.3	47.1	47.7	48.2	43.9	40.3	47.6	61.5	58.6	45.3	42.6	48.8	43.7	42.3	51.6	59.9	51.5	51.4
Tank2 Temp1 (deg C)	14.1	53.0	54.2	63.2	51.8	42.5	59.8	66.6	65.6	51.7	57.3	62.9	51.3	45.7	54.9	68.7	52.9	52.8
Tank2 Temp2 (deg C)	14.4	55.9	57.1	63.6	52.2	43.7	61.4	71.8	66.3	54.2	58.8	63.2	51.6	48.1	57.2	71.8	53.3	53.2
Tank2 Temp Avg (deg C)	14.6	52.0	53.0	58.3	49.3	42.1	56.2	66.6	63.5	50.4	52.9	58.3	48.8	45.3	54.5	66.8	52.5	52.4
Tank2 Pressure (psig)	159.8	1386.0	2709.0	3729.5	3613.7	3907.6	5719.4	7863.3	8396.8	1019.6	2476.9	3707.4	3589.6	4593.6	6210.2	8582.1	8049.5	8044.9
Tank2 Mass PVT (kg)	0.064	0.444	0.823	1.076	1.073	1.172	1.553	1.951	2.067	0.334	0.759	1.071	1.068	1.333	1.668	2.086	2.053	2.053
Tank2 Weight Scale (kg)	0.000	0.369	0.742	1.003	1.002	1.097	1.471	1.864	1.993	0.262	0.690	1.004	2.003	1.258	1.582	2.003	1.993	1.993

Source: DMS Hydrogen Laboratory

Table 30 (cont.): Selected Fill Data from Day 15 (10/23/2013)

Reading	2	13	24	35	46	58	69	80	101	112	124	135	146	158	169	180	191	198
Time (Min.)	1154	1157	1201	1205	1210	1231	1235	1240	1247	1616	1620	1624	1629	1709	1714	1717	1747	1748
Time (Sec.)	53	41	58	17	6	51	58	17	48	13	44	46	48	38	51	46	37	13
System Pressure (psig)	160.9	1386	2696.2	3966.7	4320.3	3860.3	5648	7772.3	9742.4	1046.8	2445.9	3817.3	3958.3	4532.1	6130.4	8595.5	9800.8	9801.3
Coriolis Total (kg)	0	0.757	1.529	2.086	2.09	2.18	2.902	3.646	4.077	0.522	1.347	1.974	1.998	2.4	3.025	3.824	3.975	3.975
Coriolis Adjusted (kg)	0	0.757	1.529	2.086	2.09	2.18	2.902	3.646	4.077	0.522	1.347	1.974	1.998	2.4	3.025	3.824	3.975	3.975
PVT Adjusted (kg)	0	0.734	1.461	2.013	2.015	2.123	2.839	3.599	4.01	0.528	1.352	1.986	2.012	2.429	3.069	3.883	4.002	4.001
Scale Adjusted (kg)	0	0.725	1.443	2.005	3.012	2.102	2.82	3.573	4.004	0.516	1.349	1.984	3.01	2.411	3.038	3.862	5.006	4.006

Source: DMS Hydrogen Laboratory

Installation of the HFS at DMS

The HFS was secured and crated for shipment to Sacramento following approval by DMS staff of the control charts generated at NREL. A DMS 1996 Ford F 250 4X4 extended cab pickup truck with an available cargo weight rating of 2,200 pounds was selected to house and transport the HFS.

A custom fiberglass service body manufactured by SpaceKap was purchased to enclose the truck bed to protect the HFS from wind and rain, and to provide security from theft and vandalism when the truck is parked in locations around the state. A capped, passive vent was installed at the high point of the roof of the SpaceKap to prevent any accumulation of hydrogen. The service body was installed by DMS. Parts for mounting the HFS to the bed were fabricated by Sacramento Capital Machine and Sacramento Custom Truck Accessories. Custom Truck Accessories completed the installation of the HFS to the bed of the truck. The mounting is similar to the way a fifth wheel trailer would mount to the bed of a pickup truck. The service body has windows and LED lighting that provide sufficient light and has sufficient clearance for access to all sides of the HFS. DMS staff connected the truck's electrical system to the service body. Figure 36 shows the service body mounted on the DMS truck. Figure 37 shows the interior of the service body before the HFS was installed.

Figure 36: SpaceKap Service Body Installed on DMS Truck

Photo Credit: DMS Hydrogen Laboratory

Figure 37: SpaceKap Shell Housing for the HFS

Photo Credit: DMS Hydrogen Laboratory

Figure 38: HFS Mounted in the SpaceKap Shell

Photo Credit: DMS Hydrogen Laboratory

2.3 Evaluation of Control Charts and HFS Field Testing

Challenges in HFS Design, Fabrication, and Testing

The hydrogen fuel industry and its supporting technologies are in an early stage of development. As a result, many challenges were encountered in the course of this project in the design and fabrication of the HFS. Lessons learned by DMS and NREL may be instructive for others involved with hydrogen fuel technology. Among the issues encountered were the following:

- It was recognized early in the project that the validation process and the generation of control chart data required precisely controlled quantity and flow conditions that could not be maintained in the field. In addition, this testing would interfere with the operation of a retail hydrogen station. Therefore, it was agreed that the validation and control chart data would be generated at NREL where full access and environmental control could be maintained throughout the testing period.
- Availability of on-board storage tanks was found to be extremely limited since the production of hydrogen tanks competes for manufacturing capacity with CNG tanks that are currently in high demand. It was necessary to procure used tanks of two different models in order to fabricate the HFS as scheduled. Storage tanks of 4 kg capacity were not available, so the HFS was fabricated with two 2 kg tanks.
- Procurement of the high volume stationary 70 MPa storage tank required for NREL to complete the validation and generate control chart data was delayed when the first tank ordered failed to meet quality and safety specifications during testing at the fabricator.
- The master meter standard, using a Coriolis meter, did not meet the tolerances required for Type Evaluation. It is possible that the HFS design of three combined standards compromised the performance of the master meter standard in unforeseen ways. In the future, improvements in standard design or metering technology (either Coriolis or sonic) may enable a stand-alone master meter standard to achieve the precision required for type evaluation.

Assessment of HFS Control Chart Data

Assessment of Control Charts

Each control chart was evaluated in groups of ten independent data points (independent data point equals one subgroup n=2). Each additional group of ten independent data points was evaluated against the pooled data by using the statistical F-test and Student t-test to examine the differences. Populations were pooled if both the F-test and the Student t-test passed. By evaluating the data in smaller groups, significant differences were more easily identified, along with possible problems or trends. The pooled standard deviations were used to examine the measurement uncertainty.

In the analysis of the 2 kg (35 MPa) drafts, thirty independent data points were evaluated for each procedure and plotted in one control chart. After performing the F-test and t-test for the gravimetric procedure, it was determined that only twenty data points would be used to calculate the measurement uncertainty. The statistics associated with the first 10 data points were judged unacceptable for this calculation. Since these were the first data acquired at NREL, this may have arisen from how the scales were initially used, uncertainties in the procedure, technician training and competency, or some other factor. For the PVT and master meter procedure, the F-test and t-test evaluations did allow for all thirty data points to be used in the determination of the measurement uncertainty as shown in Table 31.

Table 31: 2 kg (35 MPa) Measurement Uncertainty

Procedure	Number of Data points used	R-bar	Measurement Uncertainty
Gravimetric	20	2.8 g	2.4 g
Volume	30	18.4 g	15.5 g
Master Meter	30	144.3 g	144.4 g

Source: DMS Hydrogen Laboratory

The uncertainty of a result of a measurement may consist of several components, which may be evaluated by statistical methods or by others means. In this research, the measurement process uncertainty, calculated and evaluated through control charting, was considered as the largest contributor and used in calculating the expanded uncertainty (total uncertainty). The measurement process uncertainty was multiplied by a coverage factor, k, based on the degrees of freedom to provide a level of confidence of approximately 95 percent as shown in Table 32.

To meet the fundamental considerations of NIST Handbook 44, the expanded uncertainty must be less than 10 g (0.5 percent of tolerance). From Table 32, the gravimetric procedure is less than one-third or less than 10 g for the acceptance tolerance of the device under test, while the PVT and master meter failed this criterion.

The 4 kg (70 MPa) was evaluated using the same method as for 2 kg (35 MPa) as shown in Tables 33 and 34. For the gravimetric and master meter procedure, all thirty independent data points were used. For the volume procedure, the first ten independent data points failed the F-test and t-test and were not included in the determination of the measurement uncertainty. The results in Table 34 show that the gravimetric procedure would meet the fundamental considerations of less than 20 g while the PVT and master meter fail to meet this criterion.

Table 32: 2 kg (35 MPa) Expanded Uncertainty for a 95 Percent C.I.

Procedure	Degrees of Freedom (n-1)	Measurement Uncertainty	Coverage Factor k	Expanded Uncertainty
Gravimetric	19	2.4 g	2	4.8 g
Volume	29	15.5 g	2	31 g
Master Meter	29	144.4 g	2	288.8 g

Source: DMS Hydrogen Laboratory

Table 33: 4 kg (70 MPa) Measurement Uncertainty

Procedure	Number of Data points used	R-bar	Measurement Uncertainty
Gravimetric	30	7.9 g	7.6 g
Volume	20	17.4 g	16.8 g
Master Meter	30	174 g	170 g

Source: DMS Hydrogen Laboratory

Table 34: 4 kg (70 MPa) Expanded Uncertainty for a 95 Percent C.I.

Procedure	Degrees of Freedom (n-1)	Measurement Uncertainty	Coverage Factor k	Expanded Uncertainty
Gravimetric	29	7.6 g	2	15.2 g
Volume	19	16.8 g	2	33.6 g
Master Meter	29	170.0 g	2	340 g

Source: DMS Hydrogen Laboratory

Additional analysis was performed to examine the environmental effects on the measurements. It was determined that changes in temperature, pressure, humidity, and air density did not show any significant correlation with the testing results.

Installation and Field Testing of the HFS

The HFS was shipped to DMS in Sacramento and installed in a service body on a 1996 Ford F250 truck for field testing. An initial checkout of the HFS was conducted at the UC Berkeley Transportation Sustainability Research Center, Richmond California Field Station, shown in Figure 39. The HFS checkout was conducted to confirm the HFS maintained operational and performance integrity after shipment from NREL, installation into the truck, and a short road test. The HFS performed well during the checkout and maintained operational and performance integrity.

Several lessons were learned during the checkout:

- The setup and breakdown times need to be reduced to accomplish all tasks required a Type Evaluation at a retail station in the scheduled time.
- The relatively limited space around the HFS in the SpaceKap shell made it difficult to set up the HFS and make needed adjustments and repairs during field testing. Had a wider truck bed been available, a larger shell would have made access to the HFS easier.
- A more flexible vent configuration is necessary to reduce setup time and adapt to specific conditions at each station.
- A complete set of spare parts and tools for making field repairs on tubing, valves, and various connectors is also necessary.

Following the HFS checkout at the Berkeley Field Station, a field test was conducted at AC Transit in Emeryville, as shown in Figure 40. All drafts required for a type evaluation were completed successfully. DMS Measurement Standards Specialist III Robert (Norman) Ingram has begun testing and type evaluation of dispensers at the other public stations throughout California. This work is expected to be completed in 2014. Data from this testing is part of the working notes of DMS and is not subject to public records disclosure requests. The specific tolerance data from testing at each station will remain confidential. As appropriate, consolidated data will be shared with stakeholders and made available on the DMS website.

Figure 39: HFS Checkout at the UCB Richmond Field Station

Photo Credit: DMS Hydrogen Laboratory

Figure 40: HFS Field Testing

Photo Credit: M. Kashuba, CARB

2.4 Discussion, Recommendations and Future Work

Project Accomplishments

Development of Hydrogen Fuel Dispenser Requirements for NIST Handbook 44 Section 3.39

DMS director Kristin Macey and DMS Measurement Standards Specialist III Robert (Norman) Ingram were members of the USNWG that developed the hydrogen fuel dispenser requirements. The Working Group's draft code was adopted by the NCWM and published in the 2011 edition of NIST *Handbook 44* as Section 3.39 as a 'tentative code'.

In addition, these requirements are now included in the DMS *Field Reference Manual*[42] for future use by state and county inspectors in California.

Development of Type Evaluation, Field Test Procedure, and Checklist for Certification of Dispensers

An Examination Procedure Outline, *EPO 29*, and field test procedures for hydrogen dispensers have been developed. An EPO is a written set of instructions laying out the procedure to use when evaluating a device, in this case, a hydrogen dispenser. The NIST Weights and Measures Division has accepted *EPO 29* for future publication. A type evaluation checklist for the certification of retail hydrogen dispensers was developed and has been published in NCWM *Publication 14©.* These procedures and standards will provide a regulatory framework for the development of hydrogen infrastructure in California. DMS will publish the hydrogen device EPO as a policy document when the hydrogen device regulations become effective.

Adoption of the Kilogram as the Method of Sale for Hydrogen Fuel – NIST Handbook 130

The USNWG recommended the kilogram mass unit as the retail method of sale for hydrogen in October 2007. The proposal also included a definition for "hydrogen fuel" developed by DMS, which reads, "A fuel composed of molecular hydrogen intended for consumption in a surface vehicle or electricity production device with an internal combustion engine or fuel cell."[43] In 2010, regulations governing the method of sale of hydrogen fuel and this definition were added to NIST *Handbook 130 (Handbook 130 –* 2013 IV B 2.32 Retail Sale of Hydrogen Fuel (H). The complete text of these regulations is given in Appendix F.

Design, Construction, and Testing of Reference Standards to Conduct Evaluation of Retail Dispensers

DMS Measurement Standards Specialist III Robert (Norman) Ingram worked with a team of engineers and scientists at NREL to design, construct, and test three standards for the type evaluation of retail hydrogen dispensers. The three types of standards, gravimetric, PVT, and master meter, were combined in a single unit, the Hydrogen Field Standard, or HFS. The NREL team collected data from these standards for control charts. DMS' Principal State Metrologist Greg Boers generated the control charts and reviewed the test performance data of the HFS with Norman Ingram.

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[42] The DMS *Field Reference Manual:* http://cdfa.ca.gov/dms/publications.html, accessed Jan 10, 2020.

[43] NIST *Handbook 130 Uniform Laws and Regulations in the areas of legal metrology and engine fuel quality 2013 edition* Section 2.32.1, page 131.

Control chart data showed that the gravimetric standard met the tolerances necessary for type evaluation of retail hydrogen dispensers. This standard will be used by DMS in the type evaluation and routine performance testing of dispensers. Type evaluation testing has begun at retail stations throughout California.

Control chart data for the PVT and the master meter standards failed to meet the tolerances necessary for type evaluation of retail hydrogen dispensers. However, data from these standards will be collected as time permits when DMS conducts type evaluations and field testing. Further investigation would be needed to refine the design of the HFS to improve their performance. It is possible that design modifications and improvements in meter sensor technology could lead to the development of stand-alone PVT or master meter standard able to meet the specifications required for type evaluation for testing purposes.

Challenges, Lessons Learned, and Recommendations

The hydrogen fuel industry and its supporting technologies remain in an early stage of development. As a result, many challenges were encountered in the course of this project to fabricate standards. Lessons learned by DMS and NREL may be instructive for others involved with hydrogen fuel technology. Among the issues encountered were the following:

- There was limited availability of on-board storage tanks for the project. In part, this was because the production of hydrogen tanks competes for manufacturing capacity with CNG tanks, which are currently in high demand. The original standards design called for a 2 kg and a 4 kg tank; however, no new tanks in either size could be were available from manufacturers. As a result, two previously used 2 kg tanks were used instead substituted. Availability of hydrogen storage tanks is expected to remain limited for at least the near future. Accordingly, procurement of tanks for construction of additional field reference standards may take longer than expected.
- The Coriolis meter in the master meter standard has a limited capability to measure gas flows accurately at the high pressures and low densities encountered during test fills. The placement of the master meter standard downstream of the dispenser also contributes to in the high uncertainties in the master meter standard data. These factors would also be limitations in a stand-alone master meter standard.
- The original project plan was for DMS to collect control chart data for the standards at station locations throughout California. However, the validation process required data at both 35 MPa and 70 MPa be collected twice a day on thirty successive days. Data collection would interrupt station operation and consume a total of 8 kg of hydrogen each day. In addition, it was recognized that variability in environmental and dispenser conditions at different stations would be a significant source of error in control chart data. Accordingly, it was agreed that this work would be done at NREL's facility. In this way, full access and control over hydrogen quantity, flow, and pressure could be maintained throughout the testing period with no concerns about business disruption.
- Procurement of a stationary high volume 70 MPa hydrogen storage tank needed for validation testing of the HFS at NREL created a significant delay. The first tank ordered failed to meet quality specifications during testing at the fabricator and had to be replaced. Availability of hydrogen storage tanks, both mobile and stationary, is expected to remain limited at least in the near term. While this situation does not affect DMS operations with the HFS, it could affect fabrication of another standard.

- A larger truck bed to house the HFS, along with a larger enclosure would be desirable. The limited space around the HFS in the SpaceKap shell made it difficult to set up the HFS and make needed adjustments and repairs during field testing.

Future Work

With the successful deployment of gravimetric standard of the HFS, all of the project objectives relating to the specification and field testing of hydrogen fuel dispensers have been met. DMS now has the necessary tools to support device manufacturers and station operators in the development of hydrogen infrastructure in California. Type evaluation and field testing of dispensers throughout the state is underway. While protecting the confidential business information of device manufacturers and station operators, DMS will make the information and knowledge acquired through this testing available to stakeholders. DMS will continue to work with the CEC, CARB, and other partners to support the development of the retail hydrogen industry in California.

CHAPTER 3: Physical and Chemical Analysis of Biodiesel Fuel

Our economy runs largely on diesel power. Fuel tax figures from the California Board of Equalization show that in 2012, the state's monthly consumption of diesel fuel averaged over 217 million gallons.[44] Diesel engines have higher efficiency and greater power than gasoline engines. However, the combustion of petroleum-based diesel fuel is a leading source of GHG and toxic emissions in California. These emissions are major contributors to global warming and climate change and have many significant adverse public health impacts.

Biodiesel fuel is a renewable fuel that can supplement or replace No. 2 diesel fuel in compression ignition (diesel) engines. Although some compression ignition engines can run on pure biodiesel fuel, most often biodiesel is blended with petroleum diesel in concentrations up to 20 percent. Biodiesel has excellent lubricating properties and is used at low levels to meet the lubricity requirements of California's ultra-low sulfur diesel fuel. Biodiesel blends can significantly reduce GHG and most toxic tailpipe emissions. Increased use of biodiesel blends in California will improve air quality and reduce dependence on petroleum products. Biodiesel in concentrations up to five volume percent is allowed in diesel fuel and requires no special labeling at those levels.

The CDFA regulates the sale of transportation fuels in California. The California BPC Division 5, Chapter 14, Section 13450 requires the CDFA to establish and enforce quality specifications for compression ignition engine fuel in California. BPC Section 13450 requires the CDFA to adopt standard specifications for compression ignition engine fuels published by ASTM International (ASTM) or other ANSI-accredited standards development organization. ASTM has published standard specifications for diesel fuel (ASTM *D975*), pure (neat) biodiesel blendstock (ASTM *D6751*), and biodiesel blends between 6 and 20 volume percent biodiesel with diesel fuel (ASTM *D7467*), along with a suite of validated test methods for establishing compliance with these standards.

Currently, there are no standard specifications or validated test methods for biodiesel blends above 20 volume percent. Such specifications and test methods are needed to support commercialization of biodiesel blends with more than 20 volume percent biodiesel in California. When such specifications do not exist, the CDFA may be required to develop interim specifications. In the absence of standard specifications, transportation fuels may be sold in California only with a developmental fuel variance from the CDFA. This is currently the case for biodiesel blends of higher than 20 volume percent.

Neat biodiesel has very different physical and chemical characteristics than the hydrocarbons found in diesel fuel. Research on the application of ASTM's published tests is needed to identify methods that may be applied as written to blends above 20 volume percent and those that need modification to be applied to higher biodiesel blends.

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[44] California Board of Equalization Fuel Taxes Statistics and Reports: http://boe.ca.gov/sptaxprog/spftrpts12.htm, accessed Sept 17, 2013.

The DMS of the CDFA was contracted and funded by the CEC to evaluate existing diesel and biodiesel test methods for blends with concentrations above 20 volume percent. The blends tested were prepared from four stocks of biodiesel produced from waste cooking oil, soy oil, and a mixture of canola and safflower oils. These blend stocks were purchased from three biodiesel producers in California. They were selected as representative of biodiesel commercially available in California.

Each biodiesel blend stock was mixed with a ARB No. 2-D S15 Diesel Fuel Oil that was certified free of any biodiesel component to prepare a series of blends covering the range of 20 – 90 percent biodiesel. Each blend, along with the neat blend stocks, was tested using ASTM test methods to determine the suitability of the methods over the entire concentration range. Table 35 lists the test methods evaluated.

With two exceptions, the methods listed in Table 35 worked for all blends tested. The conditions of the distillation tests caused thermal degradation of the components of the biodiesel, resulting in failure of the tests for most of the blends. The Automatic Atmospheric Distillation method worked only for blends of 30 volume percent and lower. The Automatic Reduced Pressure Distillation worked only for B90 and neat B100. A microdistillation test method has been evaluated as an alternative for these two tests.

CDFA Senior Environmental Scientist Allan Morrison’s work with stakeholders through ASTM led to the establishment of an industry workgroup to develop the framework for standard for biodiesel blends above B20. CDFA took a lead role in this workgroup. The workgroup will further develop the data necessary to establish an ASTM Work Item that will lead to the development of a fuel standard for biodiesel blends above B20.

Table 35: ASTM Diesel Test Methods Evaluated

ASTM Test Method	ASTM Method Number	ASTM Method Title
Cloud Point	*D5773-10, D2500-09*	*Standard Test Method for Cloud Point of Petroleum Products*
Low-Temperature Flow Test (LTFT)	*D4539-10*	*Standard Test Method for Filterability of Diesel Fuels by Low-Temperature Flow Test*
Cold Filter Plugging Point (CFPP)	*D6371-05*	*Standard Test Method for Cold Filter Plugging Point of Diesel and Heating Fuels*
Flash Point	*D93-10a*	*Standard Test Method for Flash Point by Pensky-Martens Closed Cup Tester, Procedures A or C*
Atmospheric Pressure Distillation	*D86-10a*	*Standard Test Method for Distillation of Petroleum Products At Atmospheric Pressure*
Reduced Pressure Distillation	*D1160-06*	*Standard Test Method for Distillation of Petroleum Products At Reduced Pressure*
Fourier Transform Infrared Spectroscopy	*D7371-07*	*Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FTIR-ATR-PLS Method)*
Free and Total Glycerin	*D6584-10a*	*Standard Test Method for Determination of Total Monoglyceride, Total Diglyceride, Total Triglyceride, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography*
Kinematic Viscosity	*D445-10*	*Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)*
Water and Sediment Contamination	*D2709-96*	*Standard Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge*

Source: CDFA/DMS

3.1 Introduction to Biodiesel Fuel

> *"The use of plant oil as fuel may seem insignificant today.*
> *But such products can in time become just as important*
> *as kerosene and these coal-tar-products of today."*
>
> Rudolf Diesel, inventor of the diesel engine, 1912

Biodiesel and Air Quality in California

Diesel engines have higher efficiency and power than gasoline engines. However, the combustion of petroleum-based diesel fuel is a leading source of GHG and toxic emissions in California. These emissions are major contributors to global warming and climate change,[45] and have many significant adverse public health impacts.[46] [47] ARB has established ambient air quality standards to protect public health governing particulate matter, nitrogen dioxide, and carbon monoxide emitted when petroleum fuels are burned.[48] Both diesel particulates and nitrogen dioxide pose particular health threats to children and the elderly.[49] [50]

Biodiesel fuel is produced from fats and oils from plant or animal sources. A sustainable and renewable fuel, biodiesel can supplement or replace the fossil fuels used in compression ignition engines. In 2002, a joint report of ARB and the U.S. EPA compared emissions from biodiesel and low sulfur (300 ppm) petroleum diesel fuel in compression ignition engines. For neat soy biodiesel and a 20 percent soy biodiesel blend, emissions of particulate matter, carbon monoxide, and unburned hydrocarbons were significantly reduced compared to petroleum diesel fuel. In addition, sulfate emissions were nearly eliminated with 100 volume percent biodiesel because of its intrinsically low sulfur content.[51] The findings from this report are summarized in Table 36.

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[45] Energy and the Environment Explained: eia.gov/oiaf/1605/ggccebro/chapter1.html, accessed Jan 10, 2020.

[46] California Office of Health Hazard Assessment, Health effects of diesel exhaust: www.oehha.ca.gov/public_info/facts/dieselfacts.html, accessed Jan 10, 2020.

[47] Union of Concerned Scientists, Report on diesel engines and public health: www.ucsusa.org/clean_vehicles/why-clean-cars/air-pollution-and-health/trucks-buses-and-other-commercial-vehicles/diesel-engines-and-public.html, accessed Jan 10, 2020.

[48] ARB report on ambient air quality standards: arb.ca.gov/research/aaqs/caaqs/caaqs.htm, accessed Jan 10, 2020.

[49] ARB overview of diesel exhaust: arb.ca.gov/research/diesel/diesel-health.htm, accessed Jan 10, 2020.

[50] ARB overview of nitrogen oxide: arb.ca.gov/research/aaqs/caaqs/no2-1/no2-1.htm, accessed Jan 10, 2020.

[51] U.S. Environmental Protection Agency. "A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions," EPA420-P-02-001, October 2002, PDF version: https://archive.epa.gov/ncea/biofuels/web/pdf/p02001.pdf, accessed Jan 10, 2020.

Table 36: Emissions Reductions with Biodiesel Fuels

Percent Biodiesel	Particulate Matter	Carbon Monoxide	Unburned Hydrocarbons
100%	-47%	-48%	-67%
20%	-12%	-12%	-20%

Source: ARB and the U.S. EPA

In California, several legislative initiatives have established programs to reduce the use of petroleum products and mitigate their adverse health and environmental impacts. Assembly Bill 32 (Global Warming Solutions Act of 2006, Núñez, Chapter 488, Statutes of 2006) established programs in the ARB "to achieve real, quantifiable, cost-effective reductions of GHGs"[52] through a combination of market-based and regulatory actions. The CEC's Clean Transportation Program funds clean vehicle and equipment projects, research on biofuels production and the air quality impacts of alternative fuels. Following Governor Schwarzenegger's Executive Order S-1-07, the ARB implemented a Low Carbon Fuel Standard for California. The expanded use of biodiesel fuel has been identified as an important component for the success of these programs.

Pure biodiesel is generally not used directly as a transportation fuel for compression engines. Instead, it is blended with petroleum diesel fuel, with which it is completely miscible. The use of biodiesel significantly reduces GHG and tailpipe emissions of particulates and carbon monoxide. NO_x emissions from blends with high biodiesel content remain a concern. Research on ways to reduce NO_x emissions from higher concentration blends is ongoing. The specific composition of a biodiesel fuel, which is determined by the blend stock used in its production, has been shown to affect the amount of both NO_X and soot emissions.[53]

The designation "Bxx" indicates the volume percent biodiesel (xx) in a blend. The balance of the blend is a petroleum-based middle distillate fuel, typically No. 2 Diesel. For example, a blend of 90 volume percent biodiesel with 10 volume percent No. 2 Diesel is designated B90. Pure (or *neat*) biodiesel containing no added petroleum diesel is designated B100. Neat biodiesel must conform to the specifications established by ASTM International[54] (ASTM), in *D6751-12, Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels*. ASTM standards are copyrighted, and are available for purchase from the ASTM website at http://www.astm.org/Standard/index.shtml.

All engine fuels sold in California must meet the minimum state specifications described in the BPC, Division 5, Chapter 14, Sections 13450-13451, and the CCR, Title 4, Division 9, Chapter 6, Section 4148(c). DMS of the CDFA is responsible for the regulation of transportation fuels in California. The cited code sections require CDFA to adopt standard specifications for fuels that

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[52] Facts about Assembly Bill 32: http://www.arb.ca.gov/cc/cleanenergy/clean_fs4.htm, accessed Jan 10, 2020.

[53] Ng, Hoon Kiat et al, "Simulation of biodiesel combustion in a light-duty diesel engine using integrated compact biodiesel–diesel reaction mechanism," *Applied Energy* 102, 1275-1287 2013. Abstract: http://www.sciencedirect.com/science/article/pii/S0306261912005041, accessed Jan 10, 2020.

[54] Until 2001, ASTM International was known as the American Society for Testing and Materials.

are published by ASTM International or a similar consensus group. When such standard specifications do not yet exist, CDFA may develop interim specifications to be in effect pending the publication of standards by ASTM or another consensus group. ASTM currently has standard specifications for petroleum diesel (including blends containing up to five volume percent biodiesel), biodiesel blends between B5 and B20, and neat B100 biodiesel. Table 37 lists the numbers and titles of these standards.

Lacking published standard specifications, biodiesel blends greater than B20 may currently be sold in California only with a developmental engine fuel variance according to the provisions of the BPC Division 5, Chapter 14, Section 13405 and the CCR Title 4, Division 9, Chapter 6, Section 4144.[55] Such a variance may be granted by DMS for fleet use when a public benefit can be demonstrated and while a recognized consensus organization is developing standard specifications. A new ASTM working group was established at the June 2013 ASTM meeting in Montreal to develop specifications for biodiesel blends above B20. Allan Morrison of DMS is a part of this workgroup. At the December 2013 ASTM meeting, the working group decided that an industry task force should take the lead in developing a standard covering the range from B20 to B100. As a first step in this effort, engine performance data with higher blends will be collected by the task force.

Table 37: ASTM Standards for Diesel and Biodiesel Fuels

ASTM Standard Number	ASTM Standard Title	Biodiesel fuel blends
ASTM D975-10c	Standard Specification for Diesel Fuel Oils	Diesel and Diesel fuel containing up to 5 volume percent biodiesel (B5)
ASTM D7467-10	Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20).”	6 to 20 volume percent biodiesel (B6 to B20)
ASTM D6751-12	Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels	B100 (neat)

Source: ASTM International

Production and Testing of Biodiesel Fuels

The most widely used feedstock for biodiesel in the United States is soybean oil, which accounts for over two-thirds of the current domestic production.[56] Biodiesel is also produced domestically from waste cooking oil (WCO), called yellow grease in the rendering industry. Other feedstocks include plant sources such as safflower, canola, and palm oils. Tallow (rendered animal fat) is still being developed as a feedstock and is currently used on a much

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[55] Information about developmental fuel variances: www.cdfa.ca.gov/dms/programs/petroleum/developmentalfuels/developmentalfuels.html, accessed Jan 23, 2020.

[56] U.S. Energy Information Administration biofuel information PDF: www.eia.gov/biofuels/biodiesel/production/table3.pdf, accessed June 4, 2013.

smaller scale. The growing demand for biodiesel has stimulated research on potential new feedstocks, including camelina, yellow mustard, jatropha, algae, and fungi.[57] These new feedstocks are not yet commercially significant in the United States.

The terms used cooking oil and waste vegetable oil are synonymous with WCO. The ARB uses the term used cooking oil in its low carbon fuel regulations. These interchangeable terms refer to oil used in food preparation (most often frying) by restaurants, hotels, and other businesses. This oil must be replaced frequently to maintain acceptable food quality. WCO is classified as hazardous waste; its transport and disposal are subject to regulation. Typically, a recycler will acquire WCO under contract and sell it in bulk to biodiesel producers. Therefore, WCO can contain a variety of used oils from multiple suppliers and differ in composition from batch to batch.

The fats and oils in raw biodiesel feedstocks consist mostly of mixtures of various *triglycerides*. A triglyceride molecule contains three long chain carboxylic acids, known as fatty acids, because they are found in fats and oils. These fatty acids are connected by ester bonds to the hydroxyl (–OH) groups of a glycerin molecule. Fatty acids are classified base on the number of carbons and carbon-carbon double bonds in the molecule. The number of double bonds is referred to as the degree of unsaturation. A fatty acid with no double bond in saturated; with one double bond is monounsaturated and with two or more is polyunsaturated. The common fatty acids found in the fats and oils that compose the biodiesel feedstocks have 14 to 22 carbons atoms and may contain up to three double bonds. The structure of a typical monounsaturated fatty acid, oleic acid (chemical formula $C_{18}H_{34}O_2$), is shown in Figure 41, along with a generic triglyceride structure.

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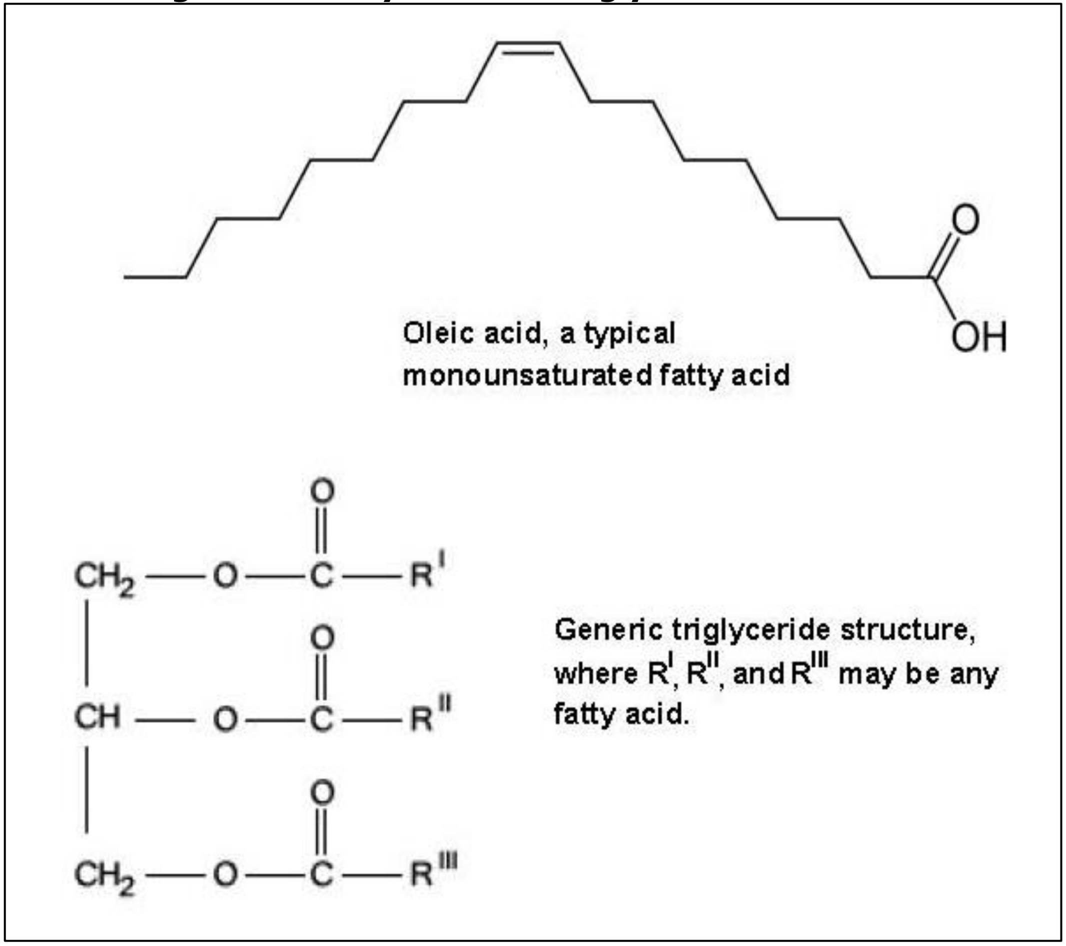
[57] Sergeeva, Y.E.; Galanina, L. A.; Andrianova, D. A.; Feofilova, E. P. (2008). "Lipids of filamentous fungi as a material for producing biodiesel fuel." Applied Biochemistry and Microbiology 44 (5): 523. abstract doi: 10.1134/S0003683808050128 dx.doi.org/10.1134%2FS0003683808050128 Accessed June 4, 2013.

Figure 41: Fatty Acid and Triglyceride Structures



Source: CDFA/DMS staff

Oleic acid is the most common monounsaturated acid found in biodiesel feedstocks. Canola oil and soy oil contain roughly 62 percent and 24 percent oleic acid by weight, respectively. Animal fats such as beef tallow and lard contain about 40 percent by weight oleic acid.[58] [59]The unsaturated fatty acid content of a feedstock determines various properties of its finished blendstock, including volatility and low temperature behavior.

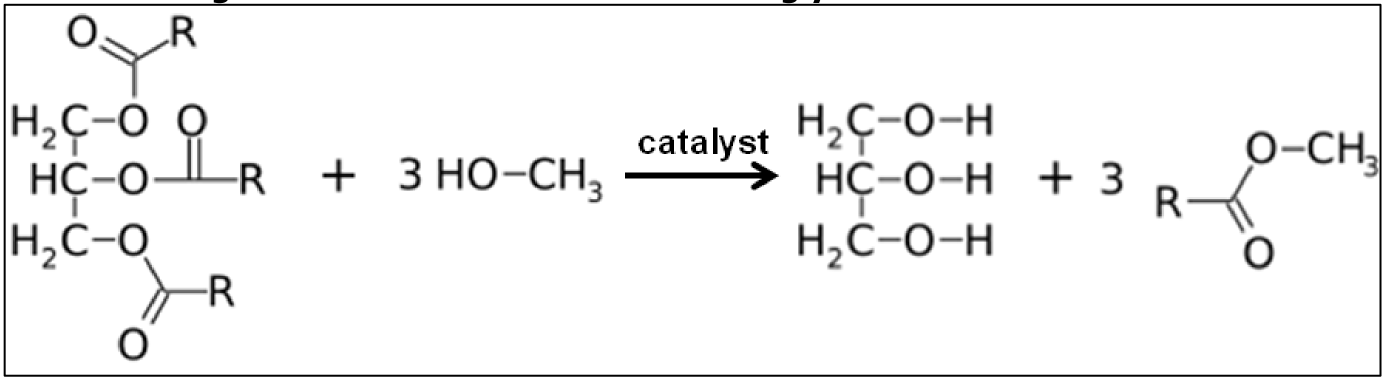
While the oils in a raw feedstock will burn in a compression ignition engine, they are much too viscous for acceptable injector and engine performance. To reduce the viscosity, the triglycerides in a feedstock are converted to a mixture of fatty-acid esters by a *transesterification* reaction. In this reaction, shown in Figure 42, the fatty acid groups are first cleaved from the glycerin molecule in the presence of a catalyst (usually a strong base such as KOH). The free fatty acid groups then react with a short chain alcohol. This reversible reaction is driven towards completion by the use of excess quantities of the alcohol. Methanol is the most common alcohol used for commercial biodiesel production, yielding a mixture of fatty

[58] Gregg, Forest, companion site for *SVO: Powering Your Vehicle with Straight Vegetable Oil*, New Society Publishers, 2008. bunkum.us/svo/fatty_acid.html, accessed July 3, 2013.

[59] National Renewable Energy Laboratory, "Biodiesel Analytical Methods August 2002–January 2004", 2009, National Biodiesel Board http://www.nrel.gov/docs/fy04osti/36240.pdf, accessed on January 23, 2020.

acid methyl esters (FAME). To isolate and purify the desired biodiesel FAME, the excess alcohol and catalyst are removed, along with the glycerin byproduct.

Figure 42: Transesterification of a Triglyceride with Methanol



R may be any straight chain fatty acid.

Source: CDFA/DMS staff

Glycerin is used primarily in the personal care products and pharmaceutical industries. In the early days of biodiesel development, the byproduct glycerin therefore had commercial value that helped to support biodiesel manufacturers. The rapid expansion of the biodiesel industry has led to a glut of glycerin on the world market, reducing its value. New uses for glycerin are being sought to absorb this excess, including its use as an engine coolant.[60] Alkyl glyceride ethers have shown promise as oxygenated diesel fuel additives.[61] Such additives may improve combustion and low-temperature performance of diesel and biodiesel fuel while improving the economics of biodiesel production.

Biodiesel is a more homogeneous mixture than petroleum diesel fuel. Its esters consist of long chains of carbon atoms ($CH_3(CH_2)_nCO_2CH_3$) with varying degrees of unsaturation (the number of carbon-carbon double bonds along the chain). Most of the chains contain 16 to 18 carbon atoms. Minor amounts of 14- and 20-carbon chains occur in some feedstocks. These fatty acid structures can be represented as XX:Y where XX is the number of carbon atoms and Y is the number of double bonds. The distribution of these chains is determined by the particular feedstock(s) used. Biodiesel from vegetable oil feedstocks consists mainly of esters of 18:1 (oleic acid) and 18:2 (linoleic acid), with lower amounts of saturated 16:0 (palmitic acid) and 18:0 (stearic acid) chains. Canola oil also contains roughly 10 weight percent 18:3 (α-linolenic acid) methyl ester. Biodiesel from animal fats, including yellow grease, has relatively higher amounts (roughly 40 weight percent) of the 16:0 and 18:0 saturated esters, along with a small amount of the 14:0 (myristic acid ester).[62]

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[60] Hudgens, R., Hercamp, R., Francis, J., Nyman, D. et al., "An Evaluation of Glycerin (Glycerol) as a Heavy Duty Engine Antifreeze/Coolant Base," SAE Technical Paper 2007-01-4000, 2007, doi:10.4271/2007-01-4000

[61] Beatrice, Carlo et al, "Technologies for energetic exploitation of biodiesel chain derived glycerol: Oxy-fuels production by catalytic conversion," in Applied Energy 102, 63-71 February 2013. Abstract: sciencedirect.com/science/article/pii/S0306261912005752, accessed July 5, 2013.

[62] Gregg, Forest, companion site for *SVO: Powering Your Vehicle with Straight Vegetable Oil* ,New Society Publishers, 2008. Fatty acids information: https://bunkum.us/svo/fatty_acid.html, accessed Jan 16, 2020.

Because the structures of these fatty acid esters are so similar, their physical and chemical properties are also similar. While the feedstock used determines the specific composition of a given biodiesel, this does not significantly affect its combustion characteristics.[63] Therefore, ASTM specifications for finished biodiesel and biodiesel blends listed in Table 37 do not differentiate among feedstocks. Some fuel parameters such as kinematic viscosity do vary according to the FAME mixture of the fuel. Modeling of biodiesel parameters based on the specific esters present is an active area of research.[64] [65]

In contrast to the mixture of FAME in biodiesel, petroleum diesel is a complex mixture of many different hydrocarbons with chain lengths of 11 to 20 carbon atoms. Up to 90 percent of a typical petroleum diesel is fully saturated, with the balance almost entirely aromatics.[66] Reflecting their structural differences, biodiesel and petroleum diesel vary significantly in their physical and chemical properties. While they are completely miscible under typical ambient conditions, the properties of a specific blend cannot be easily predicted. Blends up to B20 are in common use around the world and are well studied. Investigations of the properties of higher concentration blends are ongoing.

Use of Biodiesel Fuel in Diesel-Powered Vehicles

Automobile and diesel engine manufacturers (original equipment manufacturers or OEMs) support the expanded use of biodiesel fuels, an essential part of California programs to improve air quality and reduce petroleum dependence. To provide a warranty for their vehicles and engines, these OEMs must consider the effects of biodiesel on engine performance and maintenance. For example, early adopters of biodiesel found that its solvating properties dissolved some elastomeric materials used in seals. This problem was easily solved by switching to a different material.

On the other hand, biodiesel fuel has superior lubricating properties compared to petroleum diesel. B2 biodiesel provides enough lubricity to compensate for the low levels of sulfur mandated by California's ultra-low sulfur fuel requirements. Biodiesel also has an inherently high cetane number.

Automobiles and trucks are not the only diesel-powered vehicles converting to biodiesel fuel blends. Other on- and off-road engines, along with stationary power generator engines, are also operating with blends up to B20. School and public buses, farming and mining equipment, bus fleets, marine vessels, stationary generators, and the military are all now successfully using some blend of biodiesel fuel. Data from the National Biodiesel Board show that these

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[63] Gregg, Forest, companion site for *SVO: Powering Your Vehicle with Straight Vegetable Oil* ,New Society Publishers, 2008. Fuel property information: https://bunkum.us/svo/fuel_property.html, accessed Jan 16, 2020.

[64] Knothe, Gerhard *"Improving biodiesel fuel properties by modifying fatty ester composition,"* ***Energy Environ. Sci.***, **2**, 759-766 2009. Abstract: http://pubs.rsc.org/en/content/articlelanding/2009/ee/b903941d/unauth, accessed July 5, 2013.

[65] Giakoumis, Evangelos G. "A statistical investigation of biodiesel physical and chemical properties, and their correlation with the degree of unsaturation," *Renewable Energy* **58**, 858-878, 2013. Abstract: http://www.sciencedirect.com/science/article/pii/S0960148112004752, accessed July 5, 2013.

[66] Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services. Chemical and physical information: www.atsdr.cdc.gov/toxprofiles/tp75-c3.pdf, accessed Jan 23, 2020.

conversions were accomplished with no noticeable reduction in either engine or vehicle performance.[67] A 2006 French study for the European Biodiesel Board followed twenty-four heavy and light duty vehicles running on rapeseed (canola) B50 over a twelve-year period from 1993 to 2005. No adverse effects on engine performance or maintenance were noted compared to reference vehicles using commercial petroleum diesel fuel.[68]

Table 38 lists manufacturers currently supporting the use of B5, B20, or B100 in their engines, using the latest information available from the National Biodiesel Board.[69] This list is continually expanding, and additional manufacturers or models may have been added since the date of this report. The warranties of most manufacturers require that:

- All biodiesel blend stocks meet the specifications of ASTM *D675.*
- All finished blends meet *D975* requirements.
- All biodiesel blend stocks are sourced from a BQ-9000 Accredited Producer.

Specifications for Biodiesel Fuels

ASTM publishes standard specifications and test methods for many petroleum products and middle distillate fuels such as motor oils, gasoline, and diesel fuels. Table 37 lists the ASTM specifications for diesel and biodiesel fuels. The ASTM standards in Table 35 lists test methods to be used to demonstrate compliance with the standard specifications. These tests are published separately by ASTM. ASTM standards are regularly revised and updated. The number and letter following a standard number show the year and version of the latest release. ASTM publications are protected by copyright and may not be reproduced here. They are available for purchase from the ASTM website at astm.org/Standard/index.shtml.

ASTM test methods recommend that all test results be reported in the metric International System of Units (SI). Other units may be included in parenthesis but are meant for reference only. For clarity, only SI units are included in tables throughout this report. The text may include additional parenthetical units where appropriate.

The CDFA regulates the sale of transportation fuels in California. The BPC Division 5, Chapter 14, Section 13450 requires the CDFA to establish and enforce quality specifications for compression ignition engine fuel in California. Section 13450 requires the CDFA to adopt standard specifications for diesel fuel published by ASTM International or another recognized consensus organization. ASTM International has published standard specifications for pure (neat) biodiesel blendstock (ASTM *D6751*), and blends between 6 and 20 volume (ASTM *D7467*) percent biodiesel with petroleum diesel fuel, along with a suite of validated test methods for establishing compliance with these standards.

Currently, there are no standard specifications or validated test methods for biodiesel blends above 20 volume percent. Such specifications and test methods are needed to support

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[67] National Biodiesel Board, "Biodiesel and the U.S. Diesel Vehicle Market," 2012.

[68] P. Gateau *Twelve years of using 50% RME fuel mixture in heavy trucks and light vehicles* LOiRE2iS, https://www.ebb-eu.org/studiesreports/AEA2006_GATEAU%2050%25%2012%20years%20FRANCE.pdf, accessed Jan 17, 2020.

[69] National Biodiesel Board, OEM information: https://www.biodiesel.org/using-biodiesel/oem-information, accessed Jan 23, 2020.

commercialization of higher biodiesel blends in California. When such specifications do not exist, the CDFA may develop interim specifications. In the absence of standard specifications, transportation fuels may be sold on California only with a developmental fuel variance from the CDFA. This is currently the case for biodiesel blends of higher than 20 volume percent.

The lack of standard specifications and test methods for biodiesel blends greater than B20 is a barrier to the expanded commercial use of these blends in California. The existing biodiesel standards listed in Table 37 recognize that additional standards and test methods are needed to establish the range of blends suitable for a specific engine or application.[70]

Because biodiesel and petroleum diesel have very different physical and chemical properties, engine performance and behavior through test methods of higher blends cannot be extrapolated directly from existing data. The primary goal of this research is to support the development of standard specifications for blends between B21 and B99 by evaluating current diesel test methods over this range.

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[70] Notes in Section 4.3 of *ASTM D6751* state that,

> "NOTE 2— A considerable amount of experience exists in the U.S. with a 20 % blend of biodiesel, primarily produced from soybean oil, with 80 % diesel fuel (B20). Experience with biodiesel produced from animal fat and other oils is similar. Experience with B20 and lower blends in other applications is not as prevalent. Although biodiesel (B100) can be used, blends of over 20 % biodiesel with diesel fuel (B20) should be evaluated on a case by case basis until further experience is available.
> NOTE 3—The user should consult the equipment manufacturer or owner's manual regarding the suitability of using biodiesel or biodiesel blends in a particular engine or application."

Table 38: Vehicle Manufacturers Approving Biodiesel by Blend Concentration

OEMs Supporting B100	OEMs Supporting B20	OEMs Supporting B5
Case IH (selected models) Deutz AG Fairbanks Morse New Holland	Arctic Cat BlueBird (buses, selected models) Buhler Case Construction Equipment (selected models) Case IH (selected models) Caterpillar (Tier 4 Interim/Stage IIIb and later engines) Chrysler (in Dodge Ram for fleets) Cummins Daimler Trucks, including: · Detroit Diesel (by request) · Freightliner (Cummins engines) · Freightliner (selected Detroit Diesel engines by request) · Freightliner (Custom Chassis Corporation) · Thomas Built Buses (2010 and later models) · Western Star (selected models) Ferris Ford (2011 and later models) General Motors (2011 and later models) HDT USA Motorcycles Hino Trucks (2011 and later models) International / Navistar (conditional) Isuzu Commercial Trucks (2011 and later models) John Deere Kubota Mack Trucks Perkins (selected models) Tomcar Toro Volvo Trucks Yanmar	Audi BMW Case Construction Equipment (selected models) Case IH (all models) Chrysler (all other) Daimler Trucks, including: · Detroit Diesel · Freightliner (Detroit Diesel engines) · Western Star (all) Ford (2010 and earlier models) General Motors (2010 and earlier models) Hino Trucks (2010 and earlier models) International / Navistar (unconditional) Isuzu Commercial Trucks Mazda Mercedes Benz Mitsubishi PACCAR, including: · Kenworth · Peterbilt Perkins (all models) UD Trucks Volkswagen

Source: National Biodiesel Board (table last updated 7/26/13)

3.2 Objectives, Experimental Design and Results

The CEC and the ARB have established programs to reduce GHG and toxic emissions as well as petroleum dependence in the transportation sector. Expanded use of biodiesel fuel can make a significant contribution to these objectives. As explained in Chapter 1, CDFA must adopt enforceable fuel quality specifications before transportation fuels can be sold in California. To be legally enforceable, such specifications must be accompanied by validated test methods to demonstrate the compliance of a sample.

As discussed above, biodiesel fuel quality specifications have been published only for B100, and blends of B20 and lower. Increasing interest in biodiesel blends greater than B20 from governmental, industry and environmental groups requires research to support standard specifications for these fuels. The primary objective of this project is to evaluate the applicability of current ASTM test methods to biodiesel blends between B20 and B100. Since the physical and chemical properties of biodiesel and petroleum diesel are quite different, some of these methods may not be applicable to high concentration blends. The identification of these gaps in biodiesel test methods will be a basis for future work to develop test methods to support an expansion of biodiesel sale in California. Currently, there is limited interest within the National Biodiesel Board and engine and vehicle manufacturers for the development of specifications for high blend levels. The industry is focused on increasing the use of biodiesel blends up to B20, which may generally be accomplished without extensive engine design modifications. However, California’s Low Carbon Fuel Standard may create new opportunities for the sale of higher biodiesel blends, requiring that specifications and regulations be in place.

Project Objectives

The contract between the CEC and DMS included seven tasks for this research project:

- Develop and perform test methods to provide to federal organizations to assist with the development of national standards for biodiesel blends greater than 20 percent by volume.
- Compare the applicability of atmospheric and reduced pressure distillation techniques for high concentration biodiesel blends. Determine the optimal test conditions and concentration levels for each technique at various blend levels.
- Investigate the appropriateness of current cold temperature flow test methods for higher concentration biodiesel blends and determine the correlation between those methods. Determine which technique provides the best precision at various blend levels.
- Investigate the techniques for measuring free fatty acid and glycerin concentrations at higher concentrations. Determine which technique (i.e., Infrared spectroscopy and gas chromatography) is most appropriate and provides the best precision at various concentration levels.
- Investigate contaminant level effects on properties of fuel quality (distillation, viscosity, flash point, and cetane).
- Present CDFA findings to ASTM International to further their standards development work and/or submit as an SAE International research paper.

The evaluation of the Cetane levels was not pursued because the apparatus for measuring the cetane number was found to be prohibitively expensive. It was therefore not purchased.

Project Design

Acquisition of Biodiesel Blend Stock

For this study, B100 from three feedstocks representative of current domestic production was chosen to prepare blends for investigation. These blend stocks were soy oil, a mixture of safflower and canola oil, and WCO. The composition of WCO is more variable than other feedstocks because it is a mixture from many sources. To investigate possible differences in biodiesel blends from different WCO blend stocks, WCO from two different producers was included in this project. A small amount of each of the four raw feedstocks was also purchased to retain as a reference. Table 39 shows suppliers and amounts of the B100 and feedstocks purchased, along with the internal IDs assigned for this study. Copies of the certificates of Analysis provided with the B100 blend stocks are included in Appendix H.

American Biodiesel Inc. has operated its Community Fuels (www.communityfuels.com) refinery at the Port of Stockton, California since 2008. This plant has a capacity of 13 million gallons/year. It received BQ 9000 Producer certification in May 2012, and in March 2013 was the first producer in the country to receive BQ 9000 Laboratory certification from the National Biodiesel Accreditation Commission. Community Biofuels is a bulk supplier of biodiesel to the petroleum industry. New Leaf Biofuel (newleafbiofuel.com) is a San Diego-based producer collecting WCO from over a thousand local restaurants and businesses in southern California. Founded in 2006, New Leaf has a capacity of six million gallons/year. It operates its fleet of trucks on its B100 product. Both Community Fuels and New Leaf Biofuel receive funding from the CEC.

Imperial Western Products (www.imperialwesternproducts.com) is a diversified corporation that was founded in Coachella, California in 1966. Its Biotane Fuels Division was established in 2001, and today has a biodiesel production capacity of 12 million gallons/year. Since 2006, the Biotane Pumping Division has collected WCO from restaurants from San Diego to Fresno.

Table 39: Sources of B100 Biodiesel and Feedstocks Used

Refinery	Feedstock	DMS ID Assigned	Amount raw feedstock	Amount Neat B100
American Biodiesel Inc. (Community Fuels)	Soy oil	S-871B	1 liter	20 liters
American Biodiesel Inc. (Community Fuels)	Safflower/canola oil mixture	S-870 A/B	1 liter	20 liters
New Leaf Biofuel	WCO – Yellow Grease	A-66	2 liters	20 liters
Imperial Western Products	WCO – Yellow Grease	A-67	2 liters	20 liters

Source: CDFA/DMS staff

Analysis of the biodiesel blend stocks for fatty acid compositions was not performed as part of this project. However, earlier studies have shown that WCOs are derived largely from animal fats, and so are mostly saturated triglycerides, with the balance mostly monounsaturated. Soybean oil contains roughly 60 percent polyunsaturated triglycerides with significant amounts of saturated and monounsaturated triglycerides making up the balance. Canola oil has roughly two-thirds monounsaturated triglycerides, and one-quarter polyunsaturated triglycerides, with the balance saturated. The composition of safflower oil varies with the variety of seed used and may be either three-quarters monounsaturated or polyunsaturated. The specific composition of the safflower oil used in S870-A/B and the percentage of safflower in the blend are not known.

Acquisition of Petroleum-based Diesel

DMS staff purchased fifty-five gallons of No. 2 Diesel fuel from G&M Chevron in Placentia, CA for use throughout this study. This diesel batch was logged in as Sample #70 (2010/2011 Fiscal Year). It was tested at the CDFA Anaheim Petroleum Laboratory for conformity to ASTM standard specifications of distillation temperatures (ASTM D86) and flash point (ASTM D93). Sample #70 was also tested for any trace of biodiesel using FTIR. The diesel fuel met ASTM standard specifications and contained no biodiesel. A copy of the Anaheim Lab test report is included in Appendix H.

Use of a single lot of petroleum diesel eliminated the possibility that variability of different petroleum-diesel fuels might affect the results for this study. It is unlikely that minor differences in a compliant No. 2 diesel fuel would affect the specifications or performance of a biodiesel blend; however, that slight possibility cannot be excluded based on the work reported here.

Preparation of Biodiesel Blends

Nine test samples were prepared from each of the four B100 stocks. Using volumetric pipettes, diesel fuel from Sample #70 was used to prepare the following series covering the concentration range from B20 to B100: B20, B25, B30, B40, B50, B60, B70, B80, B90, and B100.

For convenience, the safflower/canola oil blend stock will be referred to as Saff/Can throughout this report.

Test Equipment

New equipment and supplies were needed to meet the specific objectives of the project as described above. All procurements were made following state and departmental policies and procedures. Table 40 shows the major instrumentation purchased for this project.

Table 40: Instrumentation Purchased

ASTM Test	Manufacturer	Model
D2500-09 Cloud Point and *D6371-05* Cold Filter Plugging Point	Lawler	DR4-14L
D4539-10 Low-Temperature Flow	Lawler	DR4-14L
D86-10a Atmospheric Pressure Distillation	PAC	OptiDist™ Analyzer
D1160-06 Reduced Pressure Distillation	PAC	HDV 632
D6584-10a Free and Total Glycerin	Brucker	450 GC
D7371-07 Biodiesel by FTIR	Nicolet	iS10 FTIR
D7345-08 Microdistillation	PAC	PMD 110

Source: DMS Hydrogen Laboratory

Tracking of biodiesel testing at both DMS laboratory locations (Sacramento and Anaheim) is included in the STARLIMS® laboratory information management system described in Chapter 1 of this report.

ASTM Test Methods Evaluated for This Project

The primary objective of this project was to evaluate the applicability of existing ASTM diesel test methods to biodiesel blends across the concentration range from B20 to B100. Table 41 shows the tests that were investigated in this study. (Note – Table 41 is the same as Table 35 found in the Volume 3 Summary. The table is reproduced here for convenience.)

Tests for total acid number (unreacted fatty acids), sulfur, and cetane were not included in this study. The petroleum diesel and B100 stocks used to prepare the blends met all the specifications of ASTM D975-10c and ASTM D6751-12, respectively. Therefore, any blends of these would also meet the specifications since the blending process could only dilute any free acid or sulfur impurities present. As discussed above in Chapter 1, all FAME mixtures have a higher cetane value than petroleum diesel. So, all biodiesel blends made with a compliant No. 2 diesel will necessarily exceed the minimum cetane value.

Following ASTM guidelines, all testing is reported in SI units. Instruments used to collect data for this research were configured to report in SI units. Other units may be included in parenthesis throughout this report but are meant for reference only. For sake of clarity and simplicity, only the SI °C is included in the tables and figures in this report.

All ASTM standards and test methods are subject to copyright and cannot be reproduced in this report. The standards and methods referenced here can be purchased from the ASTM website at www.astm.org/Standard/index.shtml.

Table 41: ASTM Test Methods Evaluated in This Study

ASTM Test Method	ASTM Method Number	ASTM Method Title
Cloud Point	*D5773-10, D2500-09*	*Standard Test Method for Cloud Point of Petroleum Products*
Low-Temperature Flow Test (LTFT)	*D4539-10*	*Standard Test Method for Filterability of Diesel Fuels by Low-Temperature Flow Test*
Cold Filter Plugging Point (CFPP)	*D6371-05*	*Standard Test Method for Cold Filter Plugging Point of Diesel and Heating Fuels*
Flash Point	*D93-10a*	*Standard Test Method for Flash Point by Pensky-Martens Closed Cup Tester, Procedures A or C*
Atmospheric Pressure Distillation	*D86-10a*	*Standard Test Method for Distillation of Petroleum Products At Atmospheric Pressure*
Reduced Pressure Distillation	*D1160-06*	*Standard Test Method for Distillation of Petroleum Products At Reduced Pressure*
Fourier Transform Infrared Spectroscopy	*D7371-07*	*Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FTIR-ATR-PLS Method)*
Free and Total Glycerin	*D6584-10a*	*Standard Test Method for Determination of Total Monoglyceride, Total Diglyceride, Total Triglyceride, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography*
Kinematic Viscosity	*D445-10*	*Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)*
Water and Sediment Contamination	*D2709-96*	*Standard Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge*

Source: ASTM International

Most determinations were made in duplicate, and both results are included in the tabulated data for the individual tests discussed below. Exceptions will be noted in the discussion for each test below.

Cloud Point - ASTM *D5773-10 and D2500-09*

Overview

The cloud point of a diesel fuel is one indicator of its low temperature performance. The cloud point is the temperature at which biodiesel methyl esters first begin to precipitate from solution as the fuel cools. These esters appear as a waxy material, giving the fuel a cloudy appearance. The small particles may plug filters, or sink in a storage tank, changing the liquid fuel's biocontent. The cloud point is a '*report-as-tested*'[71] property for both petroleum diesel and biodiesel fuels. An optional method for determining the cloud point of a sample visually was also tested and found to be applicable to all blend stocks over the complete blend range.

Method Summary

The four blend stocks were tested over the range of B20 to B100 according to ASTM *D5773-10 Standard Test Method for Cloud Point of Petroleum Products (Constant Cooling Rate Method)* and D2500*-09, Standard Test Method for Cloud Point of Petroleum Products (Cloud Point)*. *D5773* is an automated method, while *D2500* is a manual method. D2500 is the reference method for cloud point determination. The instrument used was a Model DR4-14L from the Lawler Manufacturing Corporation. This instrument cools a fuel sample in a series of air baths and measures light absorbance readings at each degree Celsius as the fuel is cooled. At the cloud point, the instrument detects the formation of waxy crystals by detecting a change in light absorbance readings between two sequential measurements. The cloud point is reported as the temperature at which this occurs. As a reference, the No. 2 Diesel was also tested and found to have a cloud point temperature of -16°C (3.2°F).

To evaluate the alternative non-instrumental Cloud Point method ASTM *D2500,* visual observations were made as the sample was chilled in the apparatus to detect the appearance of a cloudy haze in the sample. Using this manual method, each feedstock blend was observed to form an evenly distributed cloudy haze of wax crystals near the bottom of the test tube as the cloud point temperature was reached.

Low-Temperature Flow Test (LTFT)- ASTM *D4539-10*

Overview

The low-LTFT, ASTM *D4539-10, "Standard Test Method for Filterability of Diesel Fuels by Low-Temperature Flow Test,* is used to estimate the filterability of a fuel in diesel equipment. It is an indicator of cold weather performance, especially for heavy-duty equipment. This test determines the lowest temperature at which a fuel sample will pass through a filter under vacuum at specified conditions.

Method Summary

The instrument used was a Model 265-12L liquid-bath cooling unit from the Lawler Manufacturing Corporation. Method *D4539-10* determines the lowest temperature at which a 200 mL fuel sample passes through a 17 μm stainless steel filter within 60 seconds, under a constant reduced pressure. Measurements were made automatically at intervals of 1°C, beginning at a temperature determined by the cloud point of the fuel sample. When the fuel no longer filtered within 60 seconds, the trial was recorded as a "Failed" test. Data for each trial was recorded until two consecutive "Failed" tests were observed. The temperature of the last successful test was then reported as the "Minimum LTFT Pass Temperature."

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[71] For certain fuel quality parameters such as cloud point, ASTM standards do not give a pass/fail value or range. Instead, the value found in testing is reported for use by processors, sellers, and purchasers.

The LTFT was the last test to be run because of the large quantity of sample required by *D4539-10.* The initial supply of all B100 blend stocks was consumed by other testing. Additional stocks were purchased to conduct the LTFT on blends of stocks comparable to A-67 (Yellow Grease) and S-871 (Soy). A replenishment stock for A-67 (Yellow Grease), assigned sample ID A-67E, was purchased from Imperial Western. A replenishment stock for S-871 (Soy), assigned sample ID S-871B, was purchased from Community Fuels. A-67E and S-871B were refined in the same way as the corresponding original B100 stocks but were from different batch lots. Replacement B100 stock for Yellow Grease A-66 could not be obtained from New Leaf Biofuel. The Saff/Can blend stock S-870 A/B was a proprietary blend of biodiesel no longer produced by Community Fuels after the initial supply was exhausted. Therefore, blends of these two stocks could not be tested by the LTFT.

Because of the limited amount of blend stock available, only four blend levels were run for blend stocks of Yellow Grease A-67E and Soy S-871B: B20, B50, B80, and B100.

Cold Filter Plugging Point – ASTM *D6371-05*

Overview

The cold filter plugging point (CFPP) is another indicator of cold weather performance. This test determines the lowest temperature at which a specified volume of fuel will pass through a filter under specified conditions. The CFPP test cools the sample rapidly, in contrast to the LFTF.

Method Summary

The four blend stock blends were tested over the range B20 to B100 according to ASTM *D6371-05, Standard Test Method for Cold Filter Plugging Point of Diesel and Heating Fuels* (CFPP). The instrument used was a Model DR4-14L, from Lawler Manufacturing Corporation. The CFPP test determines the lowest temperature at which a blend passes through a 45 µm stainless steel wire mesh gauze filter within 60 seconds, under a constant reduced pressure. Testing begins at least 5°C above the cloud point of the sample, and the instrument decreases the temperature 1°C for each subsequent trial until the fuel no longer passes the test. The coldest temperature at which the fuel samples did pass through the filter was returned by the instrument as the CFPP temperature.

As a point of reference, the CFPP temperature for the No. 2 Diesel used for blending was determined to be -16°C (3.2°F) using ASTM *D6371-05*.

Flash Point - ASTM *D93-10a*

Overview

The flash point of a fuel is the lowest temperature at which there is a sufficient quantity of vapor formed to ignite under specified conditions. The flash point is an indication of the flammability hazard posed by a liquid fuel. ASTM Methods *D975-10c* and *D6751-12* set minimum flash point specifications of 52°C (126°F) and 93.0°C (199°F) for No. 2 diesel and biodiesel, respectively. In general, the FAMEs in biodiesel are significantly less volatile than the hydrocarbons in petroleum diesel.

Method Summary

Each series of blends was tested using ASTM *D93-10a*, "Standard Test Method for Flash Point by Pensky-Martens Closed Cup Tester," Procedures A or C (Flash Point). Procedure A was written for middle distillate fuels, lubricating oils, and other homogeneous petroleum products, while Procedure C was written specifically for B100 biodiesel fuel. The instrument used was the Herzog MP-330 Automatic Flash Point Analyzer.

Automatic Atmospheric Distillation – ASTM *D86-10a*

Overview

Petroleum products are mixtures of large numbers of different hydrocarbon compounds. These mixtures are characterized by the boiling point range of their constituents as measured by a batch distillation test, ASTM *D86-10a*.

The Automatic Atmospheric Distillation Test requires a means of measuring the volume percent of a sample recovered with increasing temperature as the distillation proceeds. ASTM *D86-10a* defines the parameter *T90* as the maximum vapor temperature at 90 volume percent of sample recovered. For a B20 biodiesel blend, ASTM *D7467* specifies a maximum T90 of 343°C (649.4°F). The complete blend range for all four blend stocks was tested to evaluate the suitability of the atmospheric distillation test for biodiesel blends. As discussed below, the test failed for all blends of B30 and higher.

Method Summary

All blends in each series were tested for atmospheric distillation temperatures using ASTM *D86-10a*, "Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure." The instrument used for this test was a Herzog OptiDist™ automatic atmospheric distillation unit from PAC, International. The instrument heats a fuel sample at a specified rate until its constituents have fully vaporized. The vapors are condensed in a condensation tube and collected in a receiving cylinder from which the volume percent recovered can be determined. Distillation temperatures are reported at the intervals specified by method *D86-10a*.

Automatic Reduced Pressure Distillation ASTM *D1160-06*

Overview

The FAME making up a neat biodiesel blend stock are significantly less volatile than the major fraction of the components of a conventional diesel fuel. In addition, these esters undergo thermal degradation before they can be distilled at atmospheric pressure. Therefore, a reduced pressure distillation method is used so that B100 samples will distill cleanly without excessive charring. As in the atmospheric distillation test method *D86-10a,* the temperature at which 90 volume percent of the sample is recovered is measured. This temperature is converted to the atmospheric equivalent temperature at 90 percent recovery (AET_{90}) using a formula given in *D1160-06.* The B100 specification *D6751-08* sets a maximum AET_{90} of 360°C (680.0°F) using the reduced pressure distillation test method.

Method Summary

All blends in each series were tested for reduced pressure distillation AET_{90} using ASTM *D1160-06*, "Standard Test Method for Distillation of Petroleum Products at Reduced Pressure." The instrument used was a Herzog HDV 632 automatic reduced pressure distillation unit from PAC International. The reduced pressure distillation is similar to the atmospheric distillation but with a constant vacuum applied to the sample in a sealed system to reduce the pressure. The working pressures for the test method ranged from 0.13 kPa to 6.7 kPa (1 mmHg to 50 mmHg). The instrument software converts temperature readings from the reduced pressure distillation into atmospheric equivalent temperatures (AET) using the equation published in ASTM *D1160-06*.

Biodiesel Content in Diesel Fuel by Mid Infrared Spectroscopy (FTIR) – ASTM *D7371-07*

Overview

The molecular structure of the FAME in biodiesel differs from that of the hydrocarbon constituents of conventional diesel fuel. This difference is reflected in the mid- infrared absorption spectra of biodiesel blends. The frequencies in the mid-IR region, 4000 through 650 cm_{-1}, correspond to the vibrations of molecular bonds. When the frequency of the radiation matches the frequency of a particular chemical bond, it is absorbed by the molecule, reducing the amount of energy reaching the detector. Measured over a range of wavelengths, this generates the characteristic infrared absorption spectrum of the molecule, which serves as a molecular fingerprint for organic compounds. The ester linkage of the FAMEs in biodiesel, with its two oxygen atoms, gives rise to absorption bands that are not seen in the spectra of the hydrocarbons found in conventional diesel. By calibrating against a set of standard mixes of known biodiesel content, the percent biodiesel in an unknown mix can be calculated based on the relative intensity of the absorption peaks corresponding to the oxygen-containing bonds.

In conventional absorption spectroscopy, the wavelength of light is tuned across the spectral region of interest by a filter or diffraction grating. In an FTIR spectrometer, all wavelengths are incident at once on the sample in a modulated beam that is then seen by the detector. A mathematical operation, the Fourier Transform, is used to recover the absorption spectrum from the detector signal.

Method Summary

All blends in each series were tested for biodiesel content using ASTM *D7371-07*, "Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FTIR-ATR-PLS Method)." This test method has been validated for concentrations from1to 20 volume percent biodiesel. The method states that the scope may be expanded to higher concentrations with appropriate modifications of the test conditions.

The instrument used was a Nicolet iS10 FTIR spectrometer from Thermo Scientific using a 60° ZnSe attenuated total reflectance (ATR) flow cell. A sample is introduced into the ATR cell and an infrared beam is focused on the entrance of the cell. From the attenuation of the beam, the instrument calculates the absorbance at each wavelength from 4000 through 650 cm_{-1}, giving a complete infrared spectrum of the sample fuel.

Water and Sediment Contamination – ASTM *D2709-96*

Overview

Excessive amounts of water and sediment in diesel fuel can cause corrosion, fouling and plugging of fuel-handling equipment and engines. ASTM D*2709 – 96* uses a centrifuge to separate water and sediment in a fuel sample so that the volume percent of each can be calculated. Specifications in ASTM *D7467* and ASTM *D975-10* for diesel and biodiesel set a maximum level of 0.05 volume percent of water and sediment.

Method Summary

All four neat biodiesel blend stocks were tested for undissolved water and sediment contamination using ASTM D2709 – 96, "Standard Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge." A Braun Corporation centrifuge was used for testing. Two centrifuge test tubes readable to 0.005 mL were filled with 100 mL of sample and tested at a relative centrifugal force of 800 for 10 minutes. Water and sediment were measured and reported as volume percent of total sample by centrifuge.

Free and Total Glycerin Content – ASTM *D6584-10a*

Overview

ASTM *D6584-10a* was written for the determination of glycerides and free and total glycerin in neat B100 biodiesel fuel using gas chromatography with an FID. Glycerin and glycerides are contaminants in finished biodiesel. Excessive levels may indicate production problems such as incomplete esterification or washing, or adulteration of the biodiesel. Contamination of biodiesel fuel by glycerin, either free or bonded, can cause poor engine performance because of injector fouling and the formation of deposits in the engine.

Method Summary

The four neat biodiesel blend stocks and selected blends were tested for free and total glycerin in biodiesel fuel using ASTM *D6584-10a.* This test method was developed to test neat biodiesel fuel. Glycerin is a by-product of biodiesel production and must be removed from the final FAME product mixture. The maximum values of free and total glycerin allowed in B100 fuel as published in ASTM *D6751-10* are 0.020 and 0.240 mass percent, respectively. As noted in Appendix X1.13 of ASTM *D7467-10*, "Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20)," there is no specification or test method to measure free and total glycerin in a finished biodiesel fuel blend. Hydrocarbon constituents of No. 2 Diesel fuel elute from the column at or about the same time as free glycerin, masking low levels of glycerin.

The instrument used was a Varian 450 GC from Bruker Daltonics, Inc. with a FIT. A Restek MXT Biodiesel 15-meter, 0.32 mm ID column with a 2-meter, 0.53 mm ID guard column was used. According to the test method, the range of detection for free glycerin was 0.005 to 0.05 mass percent and total glycerin was from 0.05 to 0.5 mass percent.

Kinematic Viscosity - *D445-10*

Overview

The kinematic viscosity of a fuel is a measure of its resistance to flow under shear stress and is a critical parameter for fuel delivery systems and engine efficiency. It also determines how easily the fuel can be pumped. Diesel with too low a viscosity may leak from various points in the fuel handling system or cause excessive wear. An excessively high fuel viscosity will reduce engine performance and may damage the fuel pump or filter.[72]

The kinematic viscosity of a given fuel will vary with temperature. Therefore, the kinematic viscosity is measured at 40 °C (104 °F), above typical ambient range. ASTM *D975-10c* and *D7467-10* specify a range of kinematic viscosity of 1.9 – 4.1 mm_2/s (sometimes stated as

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[72] SAE International Standard J313 Diesel Fuels Section 5.6. 2004 Handbook, Warrendale PA. 2004.

centistokes or cSt) at 40 °C for No. 2 diesel fuel and biodiesel blends up to B20 with No. 2 diesel. The FAME constituents of biodiesel have intrinsically higher kinematic viscosities than the corresponding hydrocarbon chains because of stronger intermolecular interactions arising from the polar ester bonds. The maximum kinematic viscosity for B100 as specified in ASTM *D6751-10* is 6.0 mm$_2$/s.[73]

ASTM *D975-10c* and *D7467-10* specify a maximum kinematic viscosity of diesel fuel of the 4.1 mm$_2$/s. A high biodiesel content blend might exceed this limit if it is prepared from a high viscosity B100 fuel. Such a blend must be diluted with enough petroleum diesel to meet the requirements of *D975-10c* and *D7467-10*.

Method Summary

All blends in each series were tested for kinematic viscosity using ASTM *D445-10*, *Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity).* The instrument used was a calibrated glass capillary viscometer. The sample fuel was heated to 40°C and drawn by vacuum into the capillary viscometer above the upper timing mark. The vacuum was removed and time for the sample to flow between the timing marks was recorded. Two trial times were averaged and multiplied by the calibration constant previously determined for the capillary viscometer to report kinematic viscosity in mm$_2$/s (cSt).

3.3 Results and Discussion

Cloud Point - ASTM D5773-10 and D2500-09

Results

For each blend stock, duplicate cloud point determinations were made at each blend level using the automated ASTM *D5773* test method. These results are reported in Table 42 below and are shown graphically in Figures 43-46. The applicability of the test method to all four blend stocks over the complete blend range was established. Visual observations of the samples were also made during the automated test to evaluate test method D2500-09. The results from method *D2500* matched the results obtained from the automatic instrumental method within the 2°C limit of repeatability of ASTM *D5773*-10.

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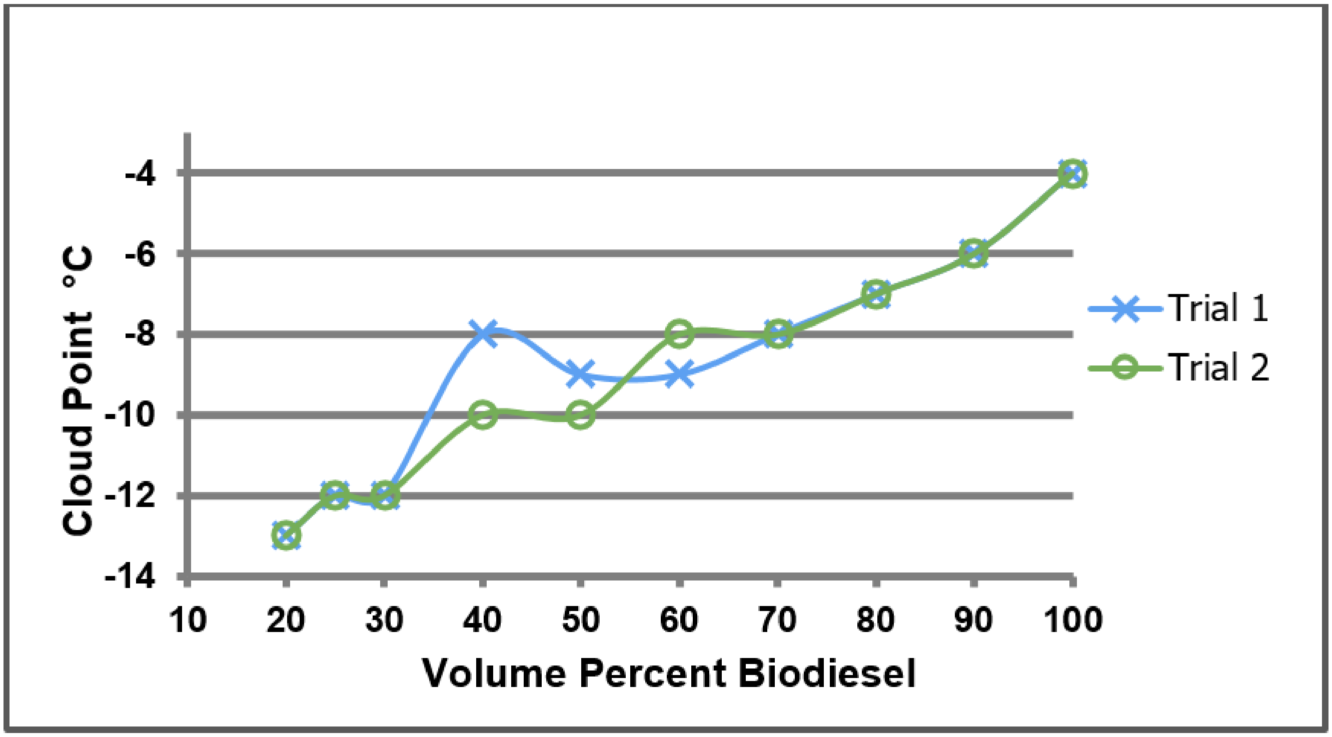
[73] The specification for B100 kinematic viscosity in Europe currently differs from that in ASTM ***D6751-10.*** The European Union standard specification EN14214 sets a range of 3.5 – 5.0 mm$_2$/s for the kinematic viscosity of B100. The higher minimum reflects the physical properties of FAME mixtures. A B100 sample with a kinematic viscosity significantly lower than 3.5 mm$_2$**/s** has likely been adulterated with a petroleum product. See Knothe et al 2005 for data on the kinematic viscosity of biodiesel constituents and mixtures.

Figure 43: Cloud Point vs. Percent Blend - S-870 Saff/Can



Source: ASTM International

Table 42: ASTM *D5773-10* Cloud Point Temperature (°C)

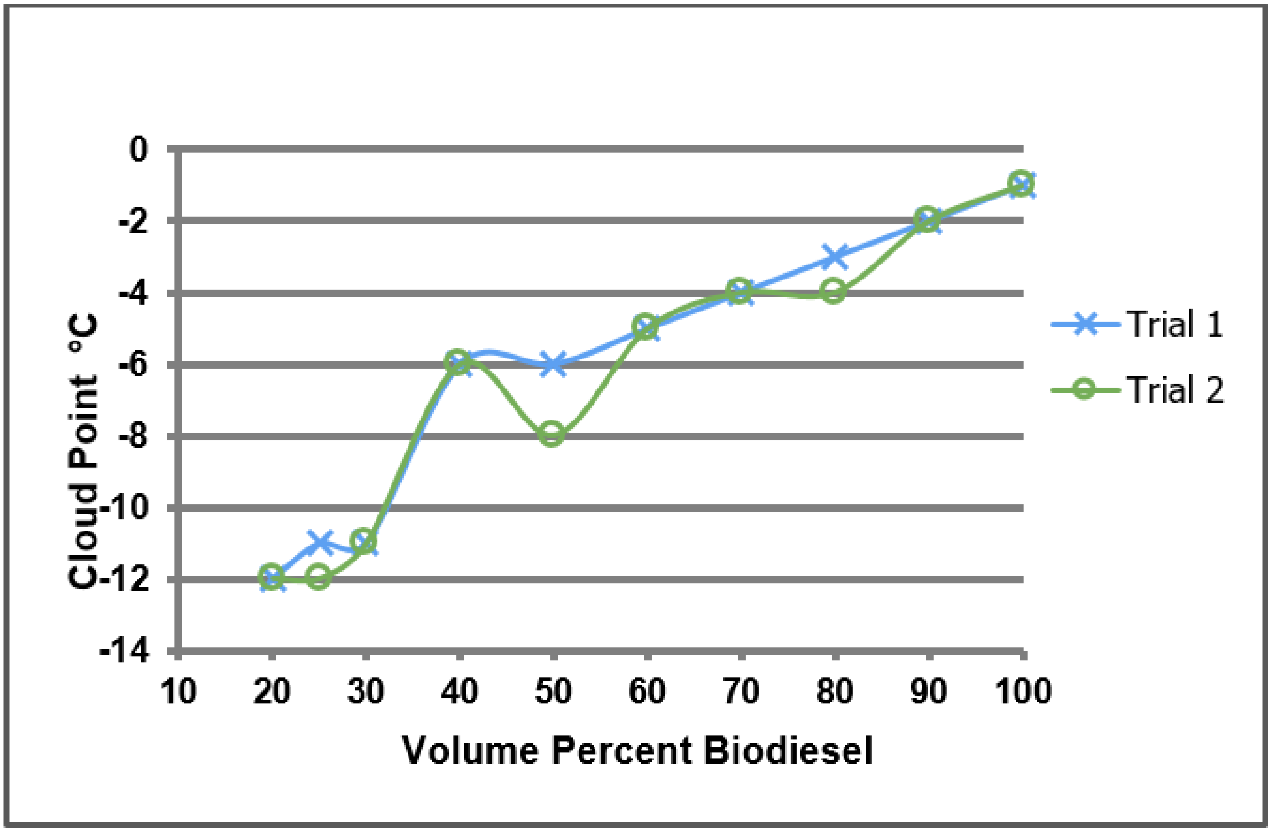
	S-870 A/B (Saff/Can)	S-870 A/B (Saff/Can)	S-871 (Soy)	S-871 (Soy)	A-66 (Yellow Grease)	A-66 (Yellow Grease)	A-67 (Yellow Grease)	A-67(Yellow Grease)
Blend	**Trial 1**	**Trial 2**	**Trial 1**	**Trial 2**	**Trial 1**	**Trial 2**	**Trial 1**	**Trial 2**
B20	-13	-13	-12	-12	-12	-12	-11	-11
B25	-12	-12	-11	-12	-11	-11	-11	-11
B30	-12	-12	-11	-11	-11	-11	-10	-10
B40	-8	-10	-6	-6	-9	-10	-9	-9
B50	-9	-10	-6	-8	-9	-9	-7	-4
B60	-9	-8	-5	-5	-6	-7	-2	-2
B70	-8	-8	-4	-4	-5	-5	-1	-1
B80	-7	-7	-3	-4	-4	-4	-1	-1
B90	-6	-6	-2	-2	-3	-3	0	0
B100	-4	-4	-1	-1	-2	-2	2	1

Source: ASTM International

Note: The cloud point of the diesel fuel used was -16°C.
The cloud point is correlated with the biodiesel concentration of the blends. The correlation appears roughly linear, but with some inflection in the graphs between 40 and 50 percent. The size of the inflection was different for the two yellow grease samples, and this may reflect differences in their composition. The -12°C value obtained for S-871 Soy B20 blend is in reasonable agreement with the -15±1°C result reported by Moser et al for a B20 soy biodiesel blend using a Phase Technology PSA 70SAnalyzer. The Moser group used an ultralow sulfur diesel with a measured cloud point of -20±1°C. The petroleum diesel used in for this work had a cloud point of -16°C.

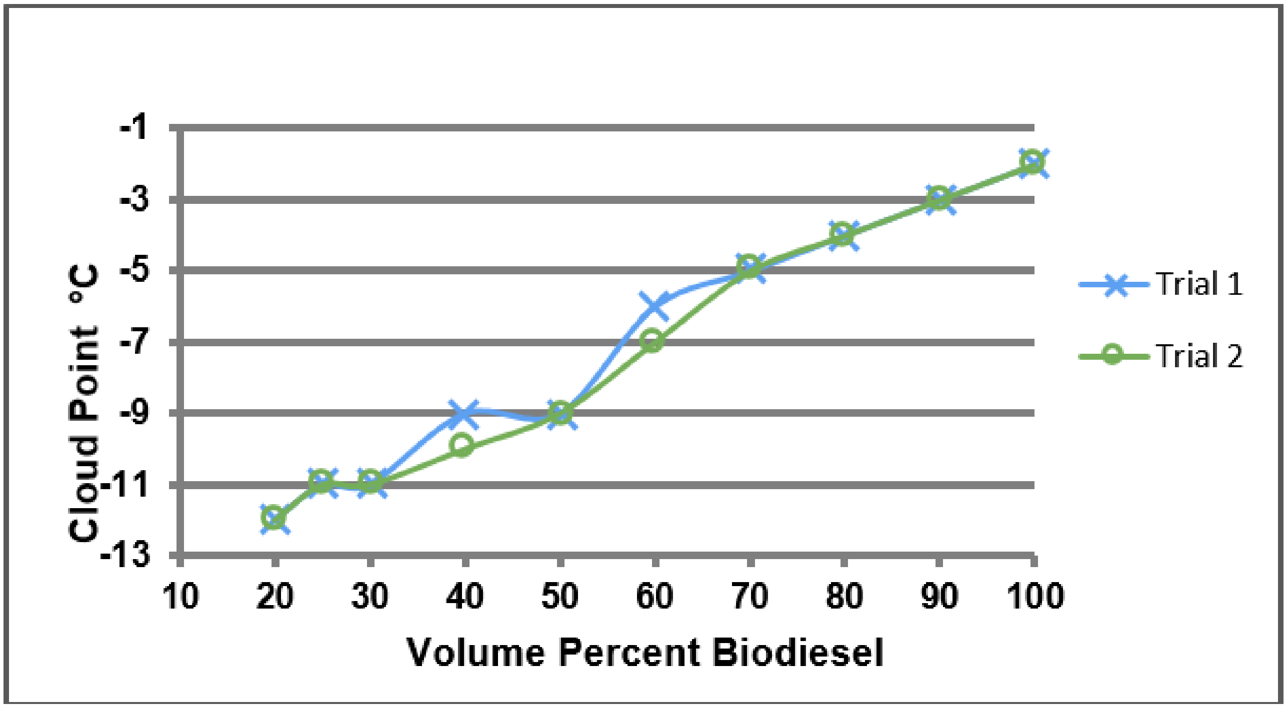
There is no evident explanation for the different behavior observed for the two Yellow Grease blend stocks. The results for blend stock A-67 may be more typical for WCO blend stocks given the variety of oils and the number of trace constituents that might be found.

Figure 44: Cloud Point vs. Percent Blend - S-871 Soy



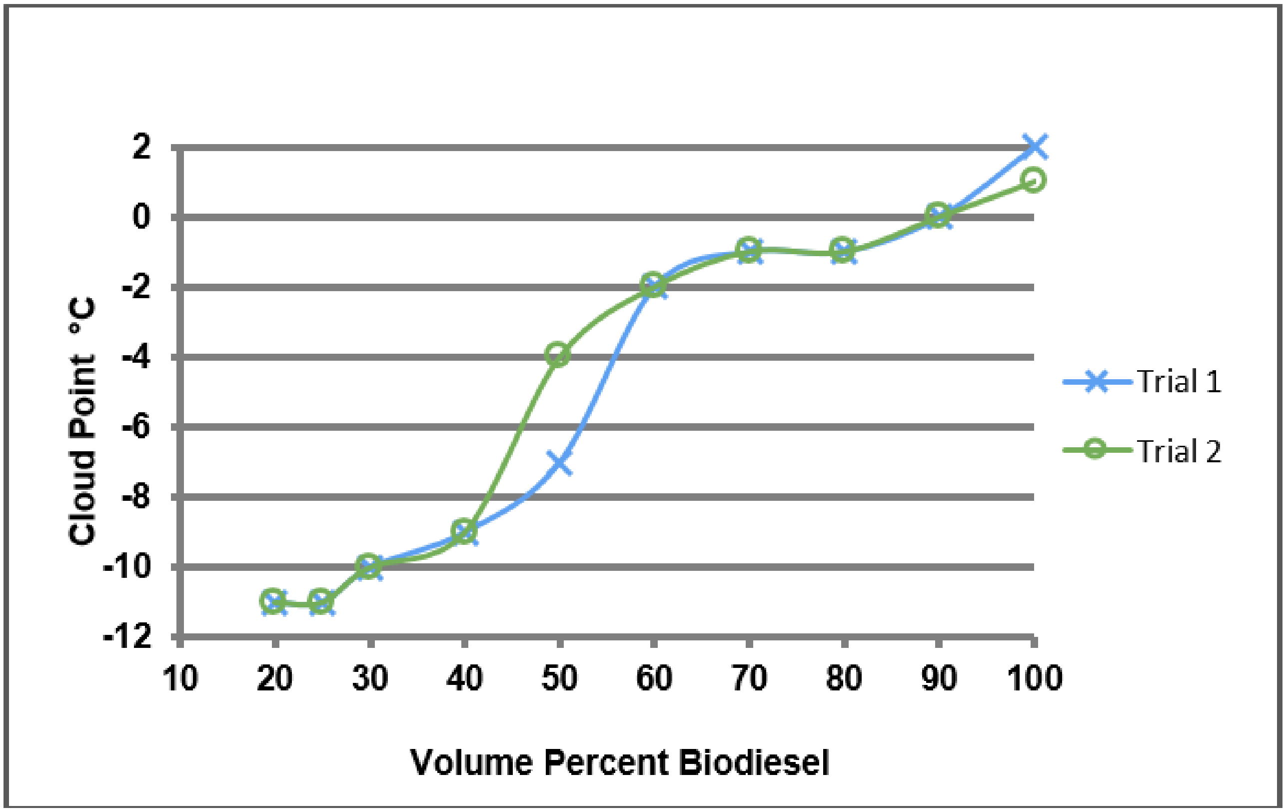
Source: ASTM International

Figure 45: Cloud Point vs. Percent Blend - A-66 Yellow Grease



Source: ASTM International

Figure 46: Cloud Point vs. Percent Blend - A-67 Yellow Grease



Source: ASTM International

LTFT Test - ASTM *D4539-10*

Results

This test method was successfully applied to the eight blends tested. Minimum LTFT Pass Temperatures in degrees Celsius and are reported in Table 43 and Figure 47.

Discussion

For the three blends of A-67E (Yellow Grease) B100 stock tested, the Minimum LTFT Pass Temperature was significantly higher than the corresponding cloud point temperatures determined using the original A-67 blend stock. This is likely due to minor differences in composition of these two yellow greases. The presence of sterol glucosides in biodiesel at very low concentrations has been associated with problems in low temperature performance even when the specifications of *D7436-10* are met.[74] [75] Such impurities are a possible explanation for these unexpected values. Sterol glucosides are found in vegetable oils, not animal fats.

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[74] Lee, Inmok, Lisa M. Pfalzgraf, George B. Poppe, Erica Powers and Troy Haines, "The Role of Sterol Glucosides on Filter Plugging", *Biodiesel Magazine,* April 6, 2007. http://biodieselmagazine.com/articles/1566/the-role-of-sterol-glucosides-on-filter-plugging/, accessed on July 17, 2013.

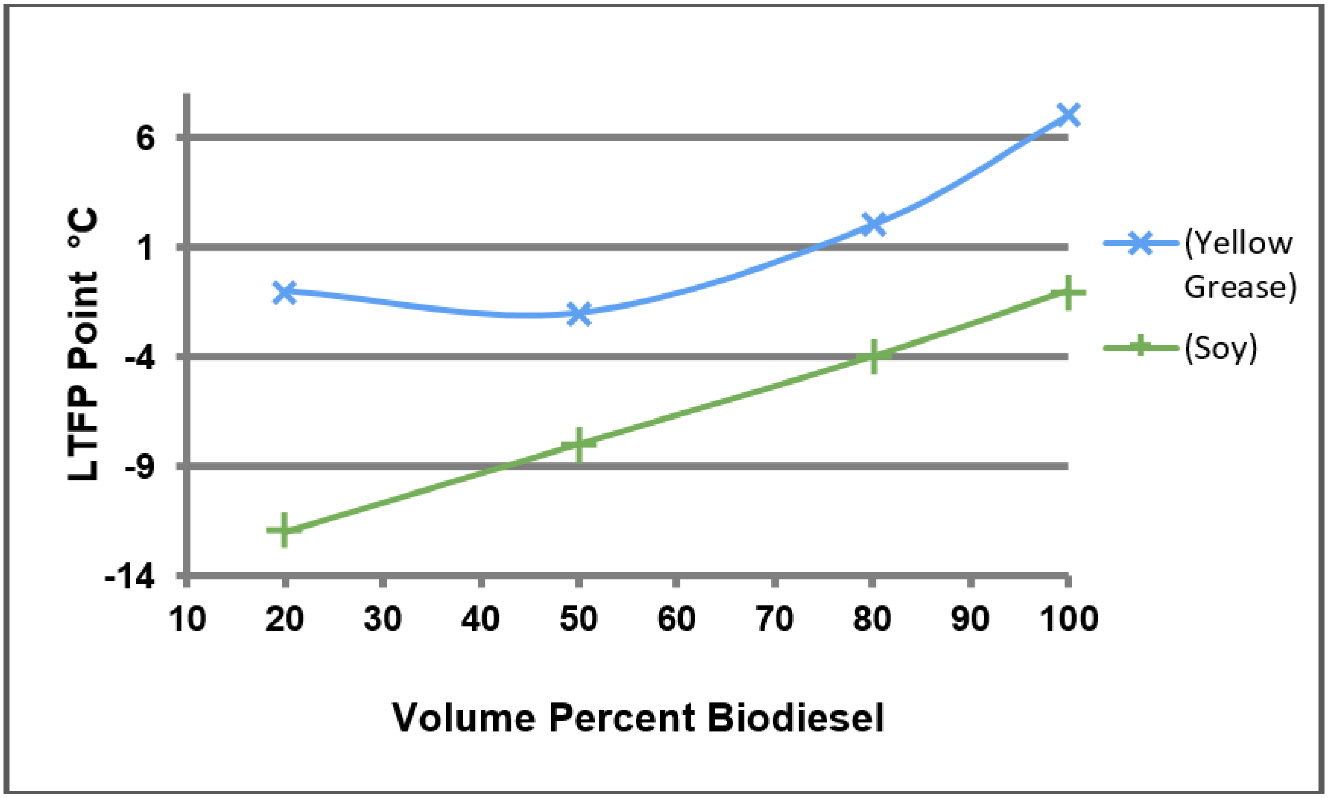
[75] Duff Keegan , Jon Van Gerpen, Brian He, National Institute for Advanced Transportation Technology, University of Idaho, *Measurement and Control Strategies for Sterol Glucosides to Improve Biodiesel Quality, Final Report KLK755*, January 2010. http://www.webpages.uidaho.edu/niatt/research/Final_Reports/KLK755_N10-02.pdf, accessed Jan 23, 2020.

Table 43: ASTM *D4539-10* Minimum LTFT Pass Temperature (°C)

Blend	A-67E (Yellow Grease)	S-871B (Soy)
B20	-1	-12
B50	-2	-8
B80	2	-4
B100	7	-1

Source: ASTM International

Figure 47: LFTP vs. Percent Blend - A-67E Yellow Grease and Soy S-871B



Source: ASTM International

However, yellow grease mixtures may contain vegetable oils used in food preparation, as well as other impurities that might lead to problems at low temperatures. Concentrations of sterol glucosides as low as 50 ppm may cause agglomeration in biodiesels. The analysis of glucosides and related natural products is complex, and well beyond the scope of this project. Future work in this area should be considered for future work.

The LTFT pass temperature is a report-as-tested parameter according to ASTM 4539-10. The LTFT temperature of a given biodiesel blend is one predictor of its low temperature performance.

Cold Filter Plugging Point – ASTM *D6371-05*

Results

The CFPP test method *D6371-05* was successfully applied to all blends in each series. Two trials were made for each blend in each series (n = 20). The data are shown in Table 44 and displayed graphically Figures 48-51 below.

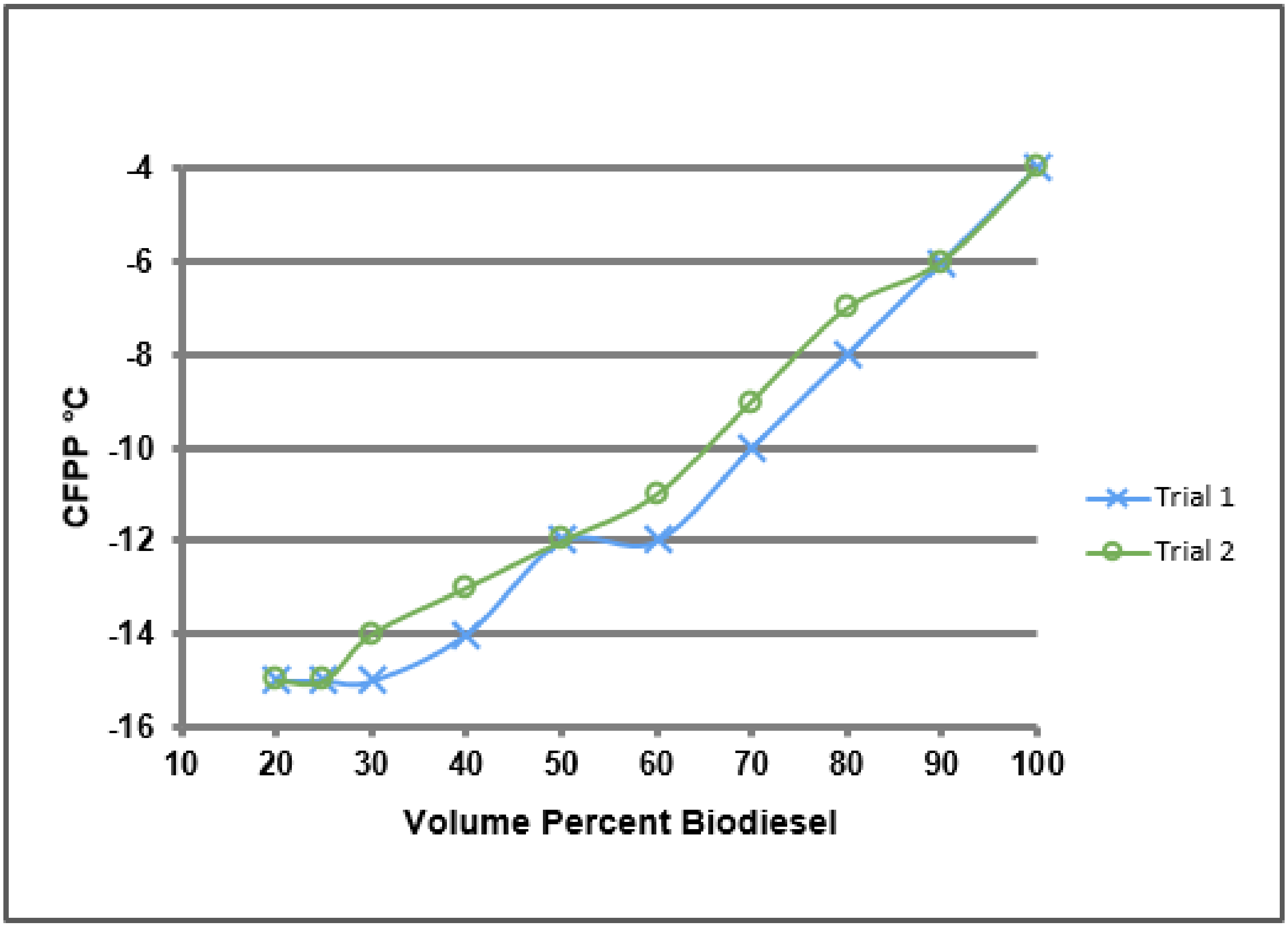
For all four blend stocks, the CFPP temperature is correlated with blend concentration. Replicate determinations for all but one sample agreed to 1°C, well within the stated repeatability of 1.76 °C of Method *6371-10*. For the 50 percent blend of Yellow Grease A-66, the difference between the replicate determinations was 2°C, equal to the method repeatability rounded to one decimal place.

Table 44: ASTM *D6371-05* CFPP Temperature (°C)

Blend	**S-871 (Soy)**		**A-66 (Yellow Grease)**		**A-67 (Yellow Grease)**		**S-870 A/B (Saff/Can)**	
	Trial 1	**Trial 2**	**Trial 1**	**Trial 2**	**Trial 1**	**Trial 2**	**Trial 1**	**Trial 2**
B20	-15	-15	-15	-15	-14	-14	-14	-14
B25	-15	-15	-15	-16	-11	-12	-13	-14
B30	-15	-14	-13	-13	-13	-12	-14	-14
B40	-14	-13	-10	-12	-12	-12	-14	-15
B50	-12	-12	-12	-10	-10	-11	-14	-14
B60	-12	-11	-9	-8	-9	-9	-14	-13
B70	-10	-9	-9	-9	-7	-7	-12	-12
B80	-8	-7	-7	-7	-6	-5	-9	-10
B90	-6	-6	-5	-6	-4	-3	-8	-9
B100	-4	-4	-4	-4	-1	-2	-7	-7

Source: ASTM International

Figure 48: CFPP vs. Percent Blend - S-871 Soy



Source: ASTM International

The CFPP temperature for the soy and A-67 yellow grease blends varied roughly linearly with concentration. The response for the A-66 yellow grease was more irregular.

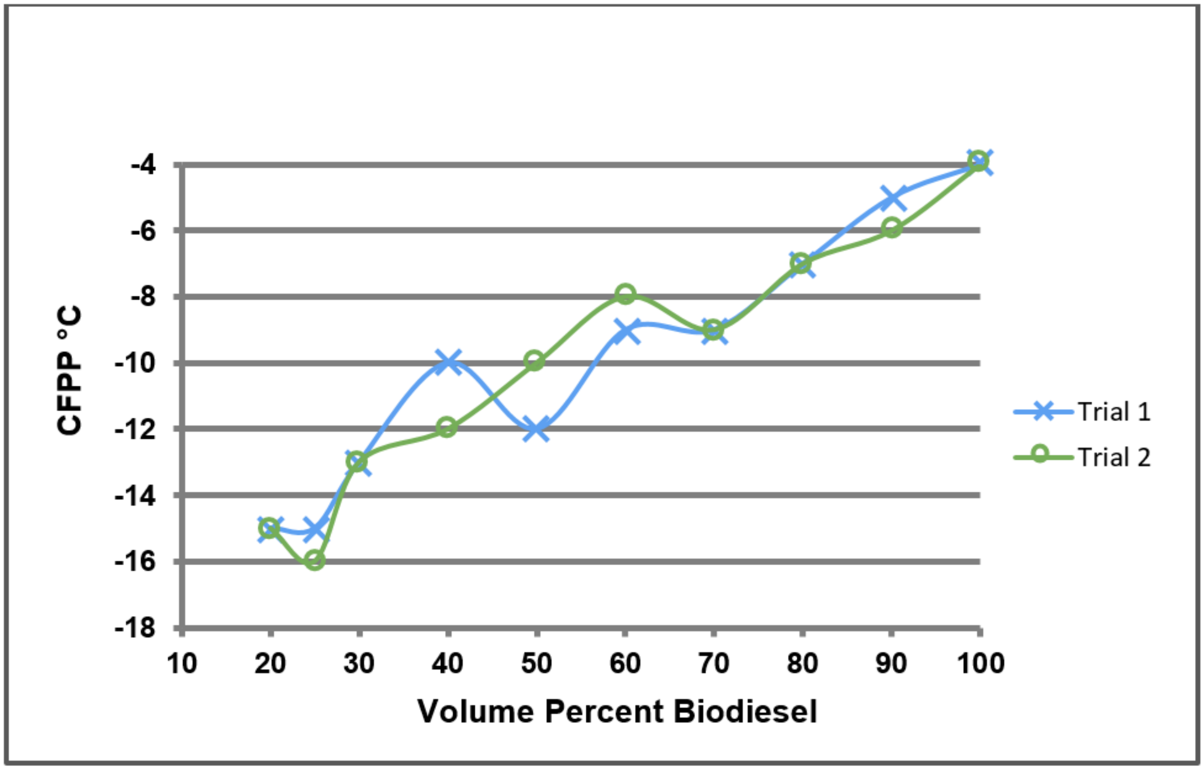
The averaged response for the safflower/canola blends showed relatively little change with concentration between 20 and 60 volume percent. Between 60 and 100 volume percent, the response was roughly linear.

Discussion

The CFPP temperature is a report-as-tested value rather than a standard specification. For petroleum diesel, the CFPP is a predictor of its filterability at low temperatures, and so is an indicator of its cold weather performance.

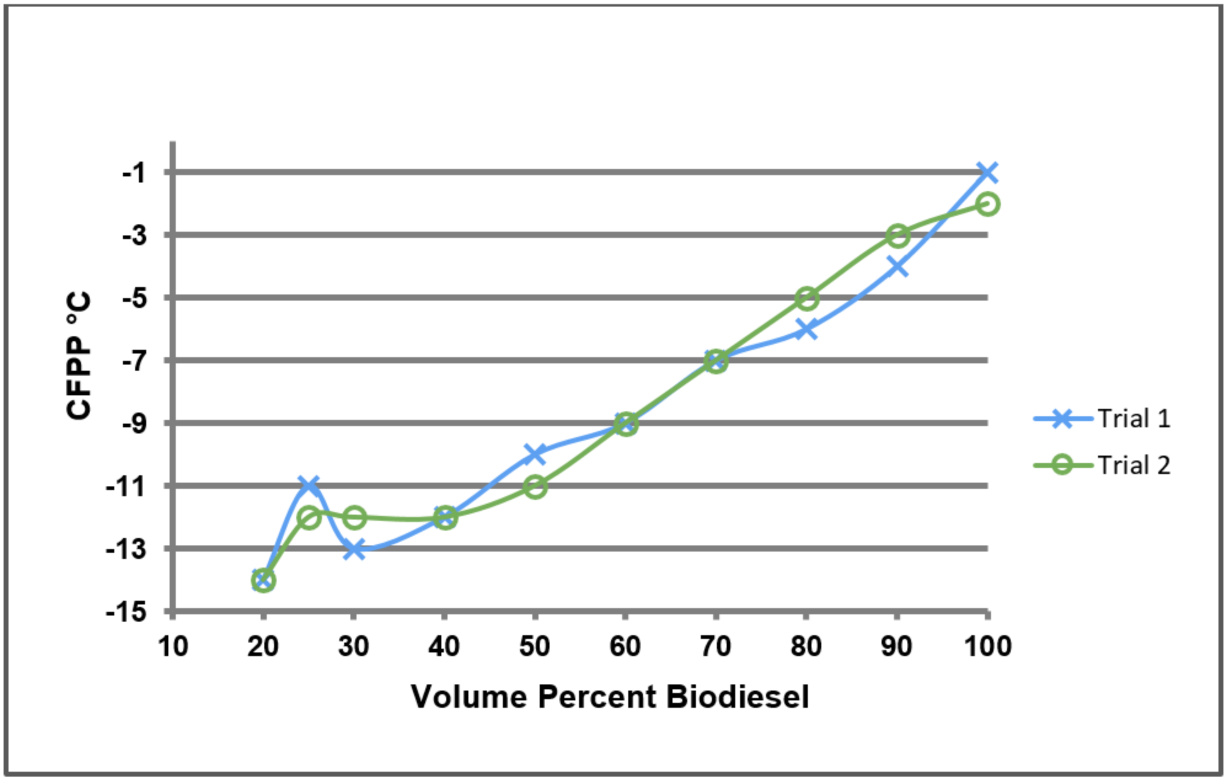
It is common practice in cold weather to blend in a portion of anti-gelling additive or No. 1 Diesel to decrease the CFPP temperature of a diesel fuel. Testing of the effects of such additives was beyond the scope of this project; however, the presence of low levels of additives would not be expected to affect the results significantly.

Figure 49: CFPP vs. Percent Blend - A-66 Yellow Grease



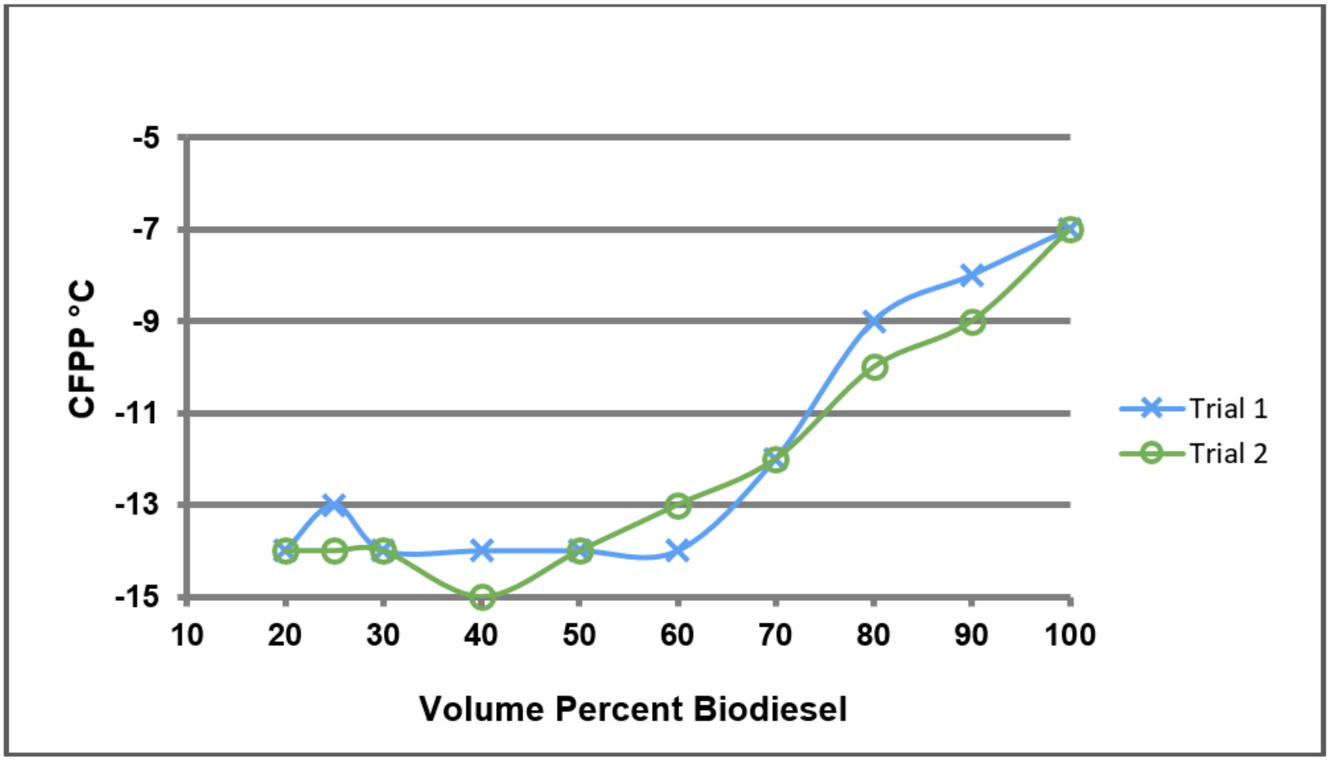
Source: ASTM International

Figure 50: CFPP vs. Percent Blend - A-67 Yellow Grease



Source: ASTM International

Figure 51: CFPP vs. Percent Blend - S-870 A/B Saff/Can



Source: ASTM International

Flash Point - ASTM *D93-10a*

Results

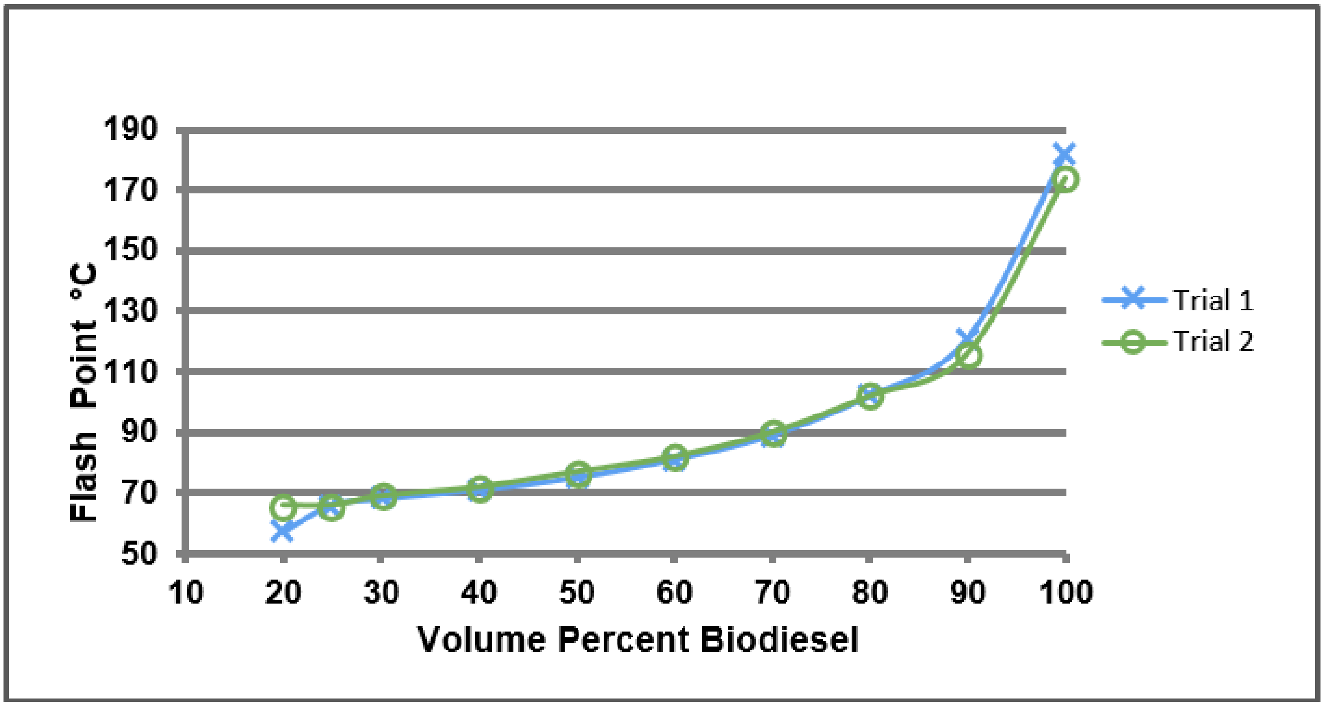
Test method *D93-10a* was successfully applied to all blends in each series. Replicate data from two trials per blend in each series (n = 20) are shown in Table 45 and Figures 52-55. All blends in each series were tested using the automated Procedure A. Procedure C was also used to test B80, B90, and B100 blends. These high biodiesel blends had flash point temperatures that approached or exceeded 100°C (212°F). There were no significant differences in the flash point temperatures obtained from Procedures A and C for B80 through B100. Automated Procedure A of ASTM *D93-10a* was adequate to safely test blends lower than B80 since flash point temperatures did not approach or exceed 100°C (212°F).

Table 45: ASTM *D93-10a* Flash Point Temperature (°C) versus Percent Biodiesel

	S-870 A/B (Saff/Can)	**S-870 A/B (Saff/Can)**	**A-67 (Yellow Grease)**	**A-67 (Yellow Grease)**	**S-871 (Soy)**	**S-871 (Soy)**	**A-66 (Yellow Grease)**	**A-66 (Yellow Grease)**
Blend	**Trial 1**	**Trial 2**	**Trial 1**	**Trial 2**	**Trial 1**	**Trial 2**	**Trial 1**	**Trial 2**
B20	57	66	65	65	64	64	61	67
B25	66	66	68	67	65	66	67	66
B30	68	69	68	68	67	67	67	69
B40	71	72	72	72	69	69	73	70
B50	75	77	76	75	72	73	76	76
B60	81	82	82	82	76	76	79	82
B70	89	90	88	89	82	83	87	87
B80	102	102	99	99	85	84	94	97
B90	121	116	115	115	104	104	115	114
B100	182	174	168	168	114	114	154	148

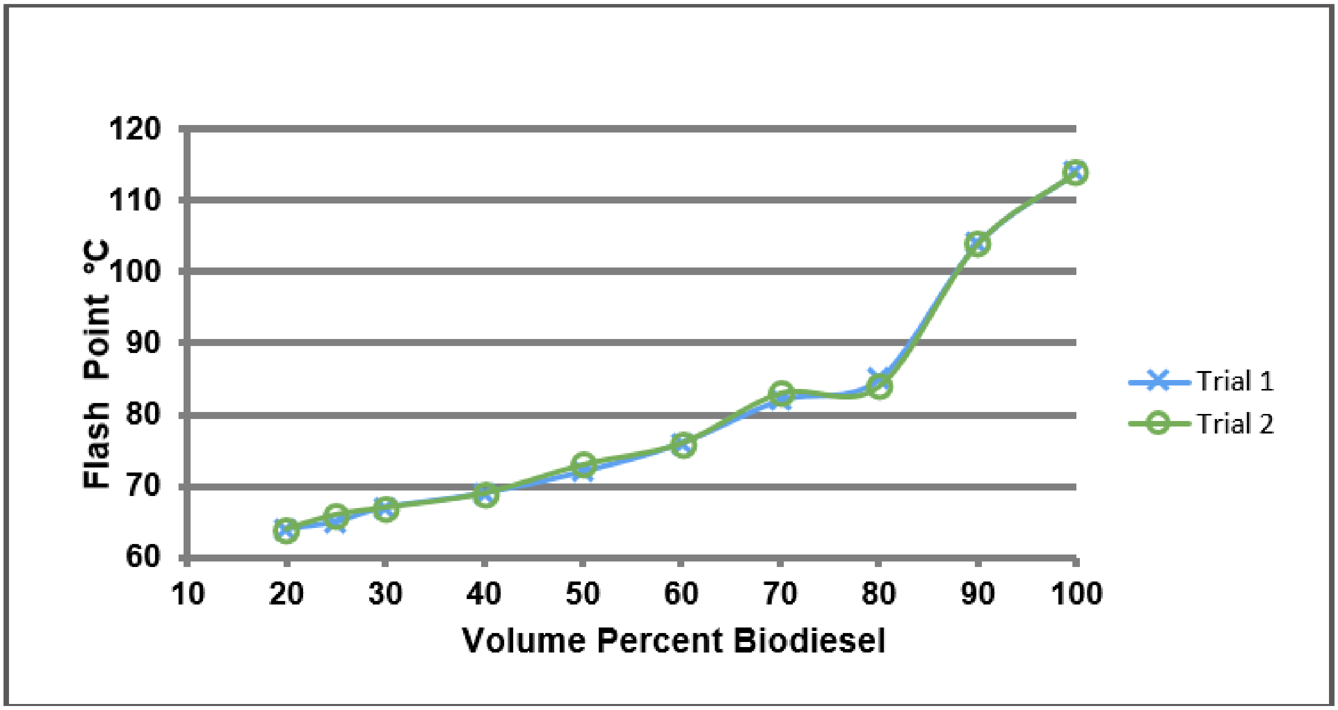
Source: ASTM International

Figure 52: Flash Point vs. Percent Blend - S-870 Saff/Can



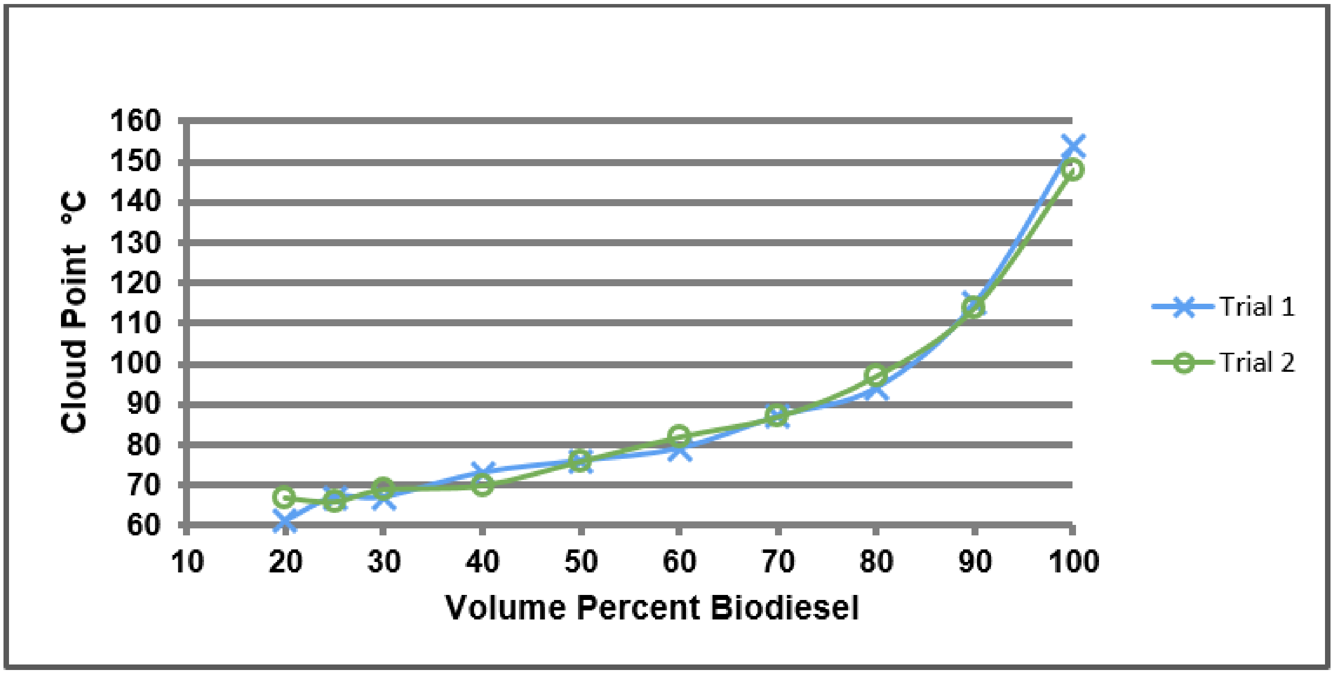
Source: ASTM International

Figure 53: Flash Point vs. Percent Blend - S-871 Soy



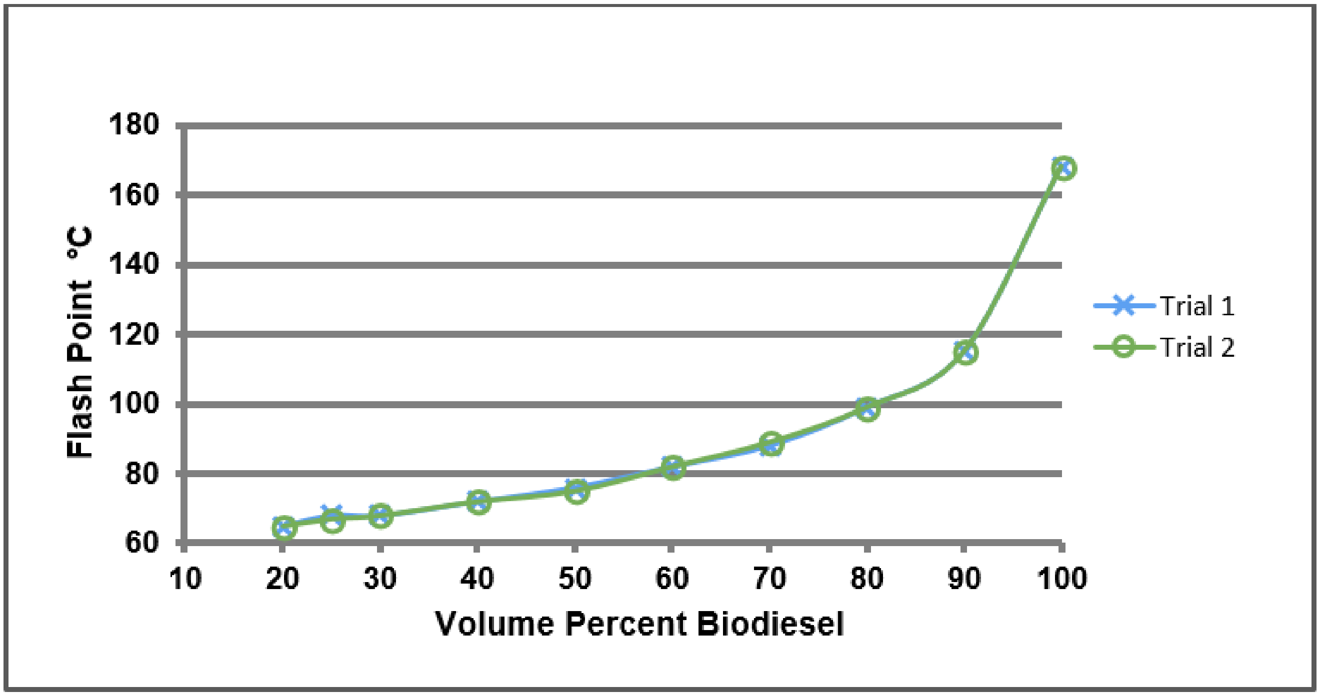
Source: ASTM International

Figure 54: Flash Point vs. Percent Blend - A-66 Yellow Grease



Source: ASTM International

Figure 55: Flash Point vs. Percent Blend - A-67 Yellow Grease



Source: ASTM International

Discussion

For all four blend stocks, the flash point increased smoothly as a function of concentration. In all cases, the response was non-linear, rising more slowly over the range 20-80 percent, and much more rapidly between 80 and 100 percent biodiesel. The repeatability of replicate determinations was within acceptable limits for most of the blends. Repeatability for Method *D93-10a* Procedure A is given as a product of the flash point in °C and a constant equal to 0.029. Over the range of observed flashpoints (roughly 60-170 °C), this formula gives repeatabilities ranging from 1.74 to 4.93 °C, or 2 to 5 °C when rounded. Most the replicate determinations fell well within this range.

Automatic Atmospheric Distillation – ASTM *D86-10a*

Results

Test method *D86-10a* was not successful for blend concentrations at or above B30 for any of the four blend stocks tested. Table 46 shows the averaged result of two trials for blends B20, B25, and B30. The T90 and final boiling point (FBP) temperatures for each blend are reported in degrees Celsius. The blend concentrations B20 and B25 of each series distilled successfully and met ASTM D86 test specifications. However, blend concentrations above B30 *cracked* (underwent thermal decomposition) during the distillation at or near a FBP of 350°C (662°F). The decomposition of these blends was indicated by white smoke filling the distillation flask and pouring into the sidearm and receiving cylinder. Immediately after white smoke appeared, the vapor temperature dropped. That behavior implied the long chain FAME broke into smaller, more volatile molecules distilling at temperatures lower than their parent esters. The automatic test continued with heavy white smoke remaining in the distillation flask and receiving cylinder. The FBP temperatures are not accurate. Moreover, the automatic optics of the instrument could not detect the final recovery volume at or near the FBP because of the lingering white smoke in the receiving cylinder. Because of these problems, the instrument could not be run in automatic mode. Data for those blends is not reported in Table 46. Instead, the entry "cracked" in the table indicates that thermal decomposition occurred for those samples.

Discussion

As the concentration of biodiesel increased, the tendency for the sample to "crack" also increased. No. 2 Diesel is less dense and made of more volatile organic compounds than biodiesel, so it vaporized at lower temperatures than the biodiesel constituents did. As the automatic atmospheric distillation progressed, the actual concentration of No. 2 Diesel decreased while the relative concentration of biodiesel increased in the remaining sample. When the vapor temperature approached or exceeded 350°C (662°F), the remaining biodiesel constituents decomposed. There is a procedure written in ASTM *D86* to report-as-tested the temperature of a sample at the point it thermally decomposes (Procedure A steps 10.13 and 10.17). However, that is not a practical method to distill high concentration blends because constant visual observation by a trained analyst would be required to detect the decomposition point of a heavy blend fuel and determine if decomposition occurred prior to the T90 recovery point. If the T90 recovery point was met or exceeded prior to decomposition, then the results could be used as reported. Otherwise, the method would still not be applicable to heavy concentration biodiesel fuel blends. Having a technician does not solve the problem of excess smoke pouring into the receiving cylinder and interfering with the optical detector that measures the recovered volume.

Table 46: ASTM *D86-10* Atmospheric Distillation Temperature (°C)

Blend	Parameter	S-870 A/B (Saff/Can)	A-67 (Yellow Grease)	S-871 (Soy)	A-66 (Yellow Grease)
B20	T90	333.7	334.2	333.8	334.3
	FBP	341.9	343.1	342.5	344.3
B25	T90	335.3	335.3	335.0	335.6
	FBP	342.0	344.0	342.1	343.8
B30 and above	T90	Cracked	Cracked	Cracked	Cracked
	FBP				

Note: All blend concentrations above B30 cracked during distillation under conditions of ASTM D86.

Source: ASTM International

Automatic Reduced Pressure Distillation ASTM *D1160-06*

Observations and Discussion

None of the blends distilled smoothly under the reduced pressure conditions of test method *D1160-06.* During testing, each sample began *bumping*, or boiling erratically and violently, and rising into the distillation column. Bumping was especially pronounced for blends below B50. This vigorous boiling brought the liquid into contact with the vapor probe, resulting in inaccurate vapor temperature readings. The boiling liquid then spilled over into the receiving cylinder, increasing the apparent distillation rate detected by the instrument, which responded by reducing the heating rate.

Measurement and control of all three of the critical distillation parameters, vapor temperature, distillation rate, and heating rate, became inaccurate. In some cases, the automatic test continued to the 70 percent recovery point in spite of the erratic readings. Pressure fluctuations in the apparatus from the bumping of the sample often exceeded the instrument's allowable limits, so that the test automatically aborted.

Multiple attempts to modify Method *D1160-06* to eliminate these problems were unsuccessful. Automatic reduced pressure distillation is not an appropriate test method for biodiesel blends.

Microdistillation, a simulated distillation method using gas chromatography, or some other technique must be used instead. Table 47 shows the average of two trials for B100, B90, B70, B50, and B40 and lighter blends in each series as AET_{90} temperatures in degrees Celsius. The average final AET temperature (AET_f) is also reported in degrees Celsius, with the corresponding volume percent recovered at a predetermined distillation stop point. An entry of "Spill-Over" is used for any blend that did not distill properly or did not conform to the specifications of the test method.

Table 47: ASTM *D1160-06* Reduced Pressure Distillation Results

Blend Level	Parameter	Distillation Temperature (°C)	Distillation Temperature (°C)	Distillation Temperature (°C)	Distillation Temperature (°C)
≤B40	AET_{90} AET_f	Spill-Over	Spill-Over	Spill-Over	Spill-Over
B50	AET_{90} AET_f	Spill-Over	355.5 425.7 @ 97%	Spill-Over	355.2 376.0 @ 97%
B70	AET_{90} AET_f	353.2 356.9 @ 97%	355.5 364.8 @ 95%	Spill-Over	356.1 368.3 @ 97%
B90	AET_{90} AET_f	353.7 359.0 @ 97%	355.5 381.1 @ 97%	353.3 358.1 @ 97%	354.3 373.4 @ 97%
B100	AET_{90} AET_f	354.9 361.3 @ 99%	356.0 363.3 @ 95%	353.9 357.7 @ 97%	355.9 362.5 @ 95%

Note: Most blend concentrations up to B70 exhibited excessive bumping and spillover. All B40, B30, B25, and B20 blends exhibited excessive bumping and spillover under the conditions specified in ASTM *D1160-06*.

Source: ASTM International

Conclusion

ASTM *D1160-06*, "Standard Test Method for Distillation of Petroleum Products at Reduced Pressure" with the Herzog HDV 632 was an adequate method to test B80 or heavier blends for all four blend stocks but was not adequate to test all blends in each series.

Trials for S-870 A/B (Saff/Can) and S-871 (Soy) began to exhibit signs of excessive bumping at B50 and B70, respectively. The Yellow Grease blend stocks A-67 and A-66 exhibited signs of excessive bumping for blends B40 or lower.

For biodiesel blends to distill properly, the conditions of the test method must accommodate the dissimilar physical and chemical characteristics of both the biodiesel feedstock and No. 2 Diesel fuel. As the concentration of biodiesel in the blend increases, the sample behaves more like neat biodiesel and becomes prone to cracking near the end of the distillation. Conversely, when the concentration of biodiesel in the blend decreases, its behavior tends toward that of diesel fuel. Low biodiesel blend samples become prone to bumping under vacuum.

Biodiesel Content in Diesel Fuel by Mid Infrared Spectroscopy (FTIR) – ASTM *D7371-07*

Results

Test method *D7371-07* worked successfully for all blends in each series. Data from three trials per sample are reported in Tables 48-51. Repeatability values in the tables are calculated using the equation given in Method *D7371*:

Repeatability (Vol. percent) = 0.01505 * (C_f + 14.905) where (C_f is the calculated concentration of the sample

Note that this equation has only been validated for blends up to B20, so these repeatability values are estimates only.

Discussion

This test method provides a quick and reliable determination of the concentration of biodiesel fuel in a blend with #2 Diesel.

ASTM *D7371-07* states that the repeatability formula published for this method is precise up to values of the differences of each of the three trials are well within the estimated acceptable repeatability values for each blend type.

To prevent sample carry-over in the FTIR cell, the manufacturer's recommendations and good laboratory practices should be followed in washing and drying the cell between samples.

Table 48: Percent Biodiesel by FTIR in Blends of S-871 Soy

Conc.	Trial 1	Trial 2	Trial 3	Average	Std. Dev	Calc. Repeat.
B20	19.78	19.83	19.96	19.86	0.09	0.523
B25	25.04	25.08	25.07	25.06	0.02	0.602
B30	30.11	30.29	30.18	30.19	0.09	0.679
B40	40.31	40.07	40.08	40.15	0.14	0.829
B50	50.71	50.78	50.67	50.72	0.06	0.988
B60	61.74	61.43	60.77	61.31	0.50	1.147
B70	71.69	71.36	70.6	71.22	0.56	1.296
B80	81.94	81.5	80.55	81.33	0.71	1.448
B90	92.1	91.27	90.33	91.23	0.89	1.597
B100	102.16	101.02	100.22	101.13	0.97	1.746

Source: ASTM International

Table 49: Percent Biodiesel by FTIR in Blends of S-870 Saff/Can

Conc.	Trial 1	Trial 2	Trial 3	Average	Std. Dev	Calc. Repeat.
B20	20.34	20.65	20.32	20.44	0.19	0.532
B25	25.49	25.59	25.55	25.54	0.05	0.609
B30	30.49	30.53	30.65	30.56	0.08	0.684
B40	41.03	40.88	41.03	40.98	0.09	0.841
B50	50.91	50.47	50.8	50.73	0.23	0.988
B60	62.3	62.13	61.94	62.12	0.18	1.159
B70	71.5	72.19	71.98	71.89	0.35	1.306
B80	82.44	82.19	82	82.21	0.22	1.462
B90	92.45	92.24	91.98	92.22	0.24	1.612
B100	102.01	101.24	101.46	101.57	0.40	1.753

Source: ASTM International

Table 50: Percent Biodiesel by FTIR in Blends of A-66 Yellow Grease

Conc.	Trial 1	Trial 2	Trial 3	Average	Std. Dev	Calc. Repeat.
B20	20.19	20.1	20.45	20.25	0.18	0.529
B25	25.18	25.1	25.26	25.18	0.08	0.603
B30	30.19	30.08	30.29	30.19	0.11	0.679
B40	40.75	40.52	40.58	40.62	0.12	0.836
B50	50.85	50.64	50.55	50.68	0.15	0.987
B60	61.41	61.12	60.7	61.08	0.36	1.144
B70	71.22	71.16	70.56	70.98	0.36	1.293
B80	81.22	81.06	80.39	80.89	0.44	1.442
B90	91.04	90.89	90.23	90.72	0.43	1.590
B100	100.94	100.72	99.97	100.54	0.51	1.737

Source: ASTM International

Table 51: Percent Biodiesel by FTIR in Blends of A-67 Yellow Grease

Conc.	Trial 1	Trial 2	Trial 3	Average	Std. Dev	Calc. Repeat.
B20	19.77	19.74	20.07	19.86	0.18	0.523
B25	25.02	25.26	25.14	25.14	0.12	0.603
B30	29.85	30.32	30.53	30.23	0.35	0.679
B40	40.15	40.2	40.76	40.37	0.34	0.832
B50	50.47	50.88	51.02	50.79	0.29	0.989
B60	61.73	62.29	60.94	61.65	0.68	1.152
B70	71.96	72.25	70.94	71.72	0.69	1.304
B80	82.13	82.56	80.98	81.89	0.82	1.457
B90	91.97	92.3	90.82	91.70	0.78	1.604
B100	102.13	102.22	100.87	101.74	0.75	1.756

Source: ASTM International

Water and Sediment Contamination – ASTM *D2709-96*

Results

Test method ASTM *D2709 – 96* was successfully applied to all blends for each of the four blend stocks. It is a quick, determinate test with little sample preparation needed. Observations from two trials per blend resulted in no measurable undissolved water or sediment in any of the blends of the four blend stocks.

Since all blend stocks were compliant with ASTM specifications, no water or sediment contamination was expected in the blends tested. To test for added water, three drops of tap water, approximately 0.10 mL, were added to a vial of neat S-871 (Soy) and tested to determine the content of undissolved water in it. The spiked sample showed approximately 0.09 volume percent of undissolved water by that test method. A vial of neat S-871 (Soy) showed no measurable signs of undissolved water or sediment.

The extension of this work to blends prepared from biodiesel stocks known to contain measurable water is recommended.

Discussion

In the laboratory, excess undissolved water or contaminants in biodiesel can interfere with the results of other test methods causing invalid data. Test method ASTM *D2709-96* should be performed before other laboratory tests to identify possible problems with other tests.

Biodiesel is hygroscopic and neat biodiesel or high concentration blends can absorb water in storage. This can lead to oxidation of the ester bonds and can cause corrosion and performance problems. High amounts of water may even support microbial growth under some circumstances. Physical damage of the pistons, piston rings, valves, valve seats, and cylinder walls in the engine may result. Testing of a blend stock by method ASTM *D2709–96* should be performed before blending with petroleum to ensure that the blend stock is within specifications.

Free and Total Glycerin Content – ASTM *D6584-10a*

Results

Test method *D6584-10a* worked for all four neat biodiesel stocks, but not the blends. Constituents of the diesel fuel co-elute with glycerin, and so interfere with its detection by GC. It is possible that a solid phase extraction method could be developed to remove the interfering components of petroleum diesel. Alternatively, it might be possible to develop a liquid-liquid extraction method to separate the more polar blend components, including glycerin, from the biodiesel blends. However, such work was outside the scope of the current project. Future work in this area is recommended.

Kinematic Viscosity - *D445-10*

Results

Test method *D445-10* worked for all blends in each series. The data are shown in Table 52 and Figure 56. The kinematic viscosity of S6, a standard reference fuel, was also measured as a check of the method. Its result was 5.695 – 5.701 mm_2/s, within the range specified in ASTM *D-445-10*.

Table 52: Kinematic Viscosity of Standard Fuel, Diesel Fuel, and Biodiesel Fuel Blends in mm$_2$/s

Blend	S6 Standard	No. 2 Diesel	S-870 Saff/Can	S-871B Soy	A-66 Yellow Grease	A-67 Yellow Grease
S6 Standard	5.695-5.701					
No. 2 Diesel		2.946				
29			3.110	3.093	3.180	3.211
B25			3.158	3.136	3.246	3.274
B30			3.215	3.190	3.357	3.350
B40			3.332	3.284	3.482	3.509
B50			3.452	3.394	3.640	3.701
B60			3.576	3.515	3.807	3.865
B70			3.708	3.633	3.995	4.076
B80			3.858	3.769	4.195	4.274
B90			4.015	3.907	4.384	4.597
B100			4.298	4.058	4.654	4.762

Source: ASTM International

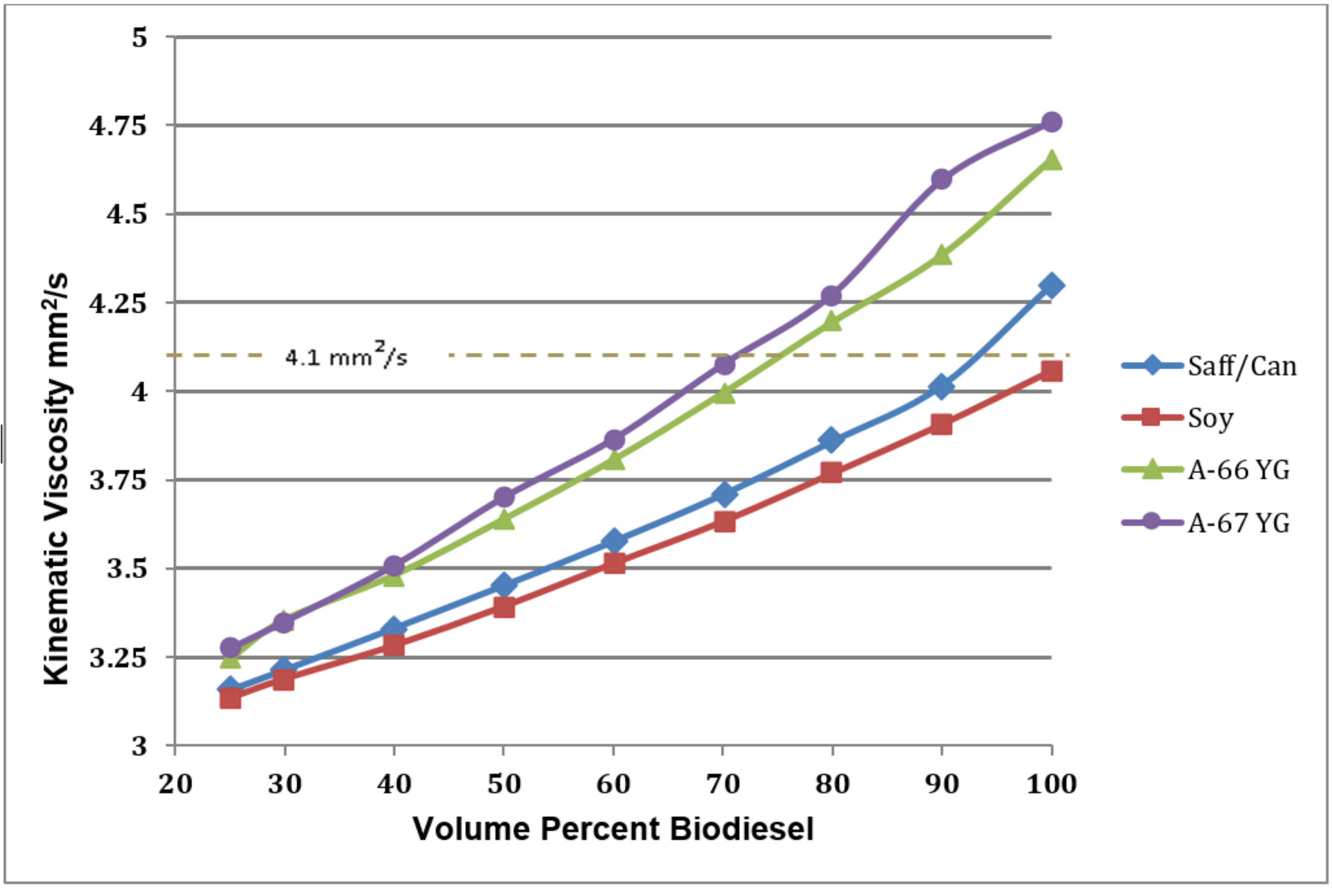
ASTM *D6751-10*T specifies a range is 1.9-6.0 mm$_2$/s for B100. The results for all of the blend stocks were well below this limit.

ASTM *D7467-10* specifies a range for kinetic viscosity of 1.9 - 4.1 mm$_2$/s for B6-B20 biodiesel fuel blends. (This is the same range allowed for No. 2 Diesel by D975-10.) This maximum value of 4.1 mm$_2$/s is shown in Figure 56 as a dashed horizontal line. Among the B100 stocks, only the soy fell below this limit. The values for the B80 and B90 yellow grease blends were also above the maximum allowed in the specifications.

Conclusion

This method was quick and determinative for testing kinematic viscosity of all blends of all four biodiesel stocks. Based on the data collected in this study, the ASTM *D6751-10* specification of kinematic viscosity may be applied to all blends in each series. The kinematic viscosity values increased proportionally as blend values increased throughout each series. Higher viscosity values correlate with larger droplet sizes in fuel injectors and may add excessive coking in the cylinder or increased particulate matter in the emissions of the engine.

Figure 56: Kinematic Viscosity of Blends



Source: ASTM International

Microdistillation ASTM *D7345-08*

Neither ASTM *D86-10* nor ASTM *D1160-06* was found to be applicable for the full range of biodiesel blends. Alternate distillation methods have been developed to address the limitations of the existing distillation test methods. New distillation instruments have been developed that use different methods of detection and are not subject to the limitations of the *D86-10.* For example, addition of a foam sensor has been used to allow more sensitive automatic temperature control to minimize bumping in blend samples. However, based on the results described in sections 3.5 and 3.6 above, it is unlikely that such modifications will be sufficient for the analysis of the full range of biodiesel blends.

Microdistillation ASTM *D7345-08* is an alternate method for both diesel and B100 blendstocks, but it has not been evaluated for biodiesel blends. DMS purchased a Model 110 Microdistillation instrument from PAC in December 2013. This instrument was tested on a limited number of blends to determine if microdistillation might work for biodiesel blends.

Preliminary results from this evaluation are very encouraging. Sample reports of the distillation profile for the B30 Yellow Grease A-67 blend and the B50 Soy blend are reproduced in Tables 53 and 54. These samples could not be analyzed by either atmospheric pressure or reduced pressure distillation. In the tables, IBP and FBP are initial and final boiling points, respectively.

Table 53: Microdistillation of B30 Yellow Grease

% Recovered	**Temp. ° C**
IBP	186.0
5%	211.4
10%	225.5
20%	246.4
30%	266.6
40%	284.6
50%	299.0
60%	311.4
70%	321.8
80%	330.6
90%	342.6
95%	350.7
FBP	354.2
%R	97.7
%r	1.9

Source: ASTM International

Table 54: Microdistillation of B50 Soy

% Recovered	Temp. ° C
IBP	195.7
5%	223.1
10%	239.0
20%	263.8
30%	288.5
40%	304.6
50%	316.8
60%	325.3
70%	331.6
80%	336.9
90%	344.1
95%	348.2
FBP	348.7
%R	97.7
%r	1.9

Source: ASTM International

3.4 Discussion, Recommendations and Future Work

The suite of existing ASTM test methods for diesel and biodiesel fuels has been evaluated over the range B20 to B100 for four blend stocks, which represent the primary biodiesel feedstocks in production today (soy oil, canola oil bended with safflower oil, and WCO). With the exception of the distillation methods and the Low Flow Temperature Test (LFTT) *D4539-10*, all methods were found to be applicable to all of the blend stocks over the complete concentration range. The data for the LFTT are incomplete only because the available sample to run this test was depleted. *D4539-10* ran successfully on all the samples for which it could be tested (see Section 3.2 above). Since this test is based on the physical properties of a fuel sample, it would be expected to work for all other biodiesel blends. Finishing the testing of *D4539-10* is recommended as part of future work on the analysis of biodiesel blends.

As discussed in sections 3.5 and 3.6, the distillation methods ASTM *D86-1 and D1160-06* are not applicable to a useful range of biodiesel blends. Microdistillation method *D7345-08* is a promising alternative method based on the limited results available. Complete testing of

D7345-08 for different blendstocks over the full blend range is recommended as part of future work.

Table 55 summarizes the results of this work for all methods tested. We conclude that the ASTM methods tested could be used to support the development of new ASTM standard specifications for biodiesel blends in the concentration range 20 – 100 volume percent. In turn, such standards could support an expanded market for biodiesel by providing enforceable quality standards.

The results of this project suggest that these test methods would be equally applicable to blends from other feedstocks that are similar to those tested, such as flaxseed and cottonseed oils. Currently, there is very little biodiesel produced domestically from such sources. However, they may become more important in the future, at least regionally. Other less familiar feedstocks such as jatropha are currently under investigation or development internationally and may become more important in the future.

Feedstocks such as palm oil and coconut oil contain predominantly saturated fatty acids, and so are significantly different from those tested in this project. It is likely that the methods tested would apply to blends of these feedstocks as well. Palm oil and coconut oil are both important feedstocks overseas and may in the future be traded internationally. The verification of the applicability of test methods to blends of these feedstocks is recommended for future work.

Polyunsaturated fatty acid esters with four or more double bonds are among the components that are of concern in biodiesel blends. Not only are these compounds relatively high boiling, they are less stable than the more saturated major components and so may cause problems in stored fuel. The European biodiesel specification *EN14214-2008* specifies a maximum concentration of 1 percent for these high polyunsaturated esters. While current ASTM standards do not include a specification, it is possible that future revisions will be normalized with international standards. Polyunsaturated esters are readily amenable to analysis by GC with FID or MS detection. FTIR methods have also been proposed. European method CSN EN 15779[76] [77] uses GC to determine the four most important polyunsaturated esters. This method has been validated over the concentration range 0.6 percent - 1.5 percent.[78] Future revisions of the method are expected to extend this validation range. It is possible that either GC or FTIR techniques could be simultaneously applied to the determination of glycerin and

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[76] Purchase CSN EN 15779: www.en-standard.eu/csn-en-15779-petroleum-products-and-fat-and-oil-derivates-fatty-acid-methyl-esters-fame-for-diesel-engines-determination-of-polyunsaturated-4-double-bonds-fatty-acid-methyl-esters-pufa-by-gas-chromatography/, accessed Jan 23, 2020.

[77] McCurry, James D. Agilent Application Note EN15779 – Gas Chromatographic Analysis of Polyunstaruated FAME in Biodiesel Made from Algae and Marine Oils, 2011. Digital Analysis: www.chem.agilent.com/Library/applications/5990-8875EN.pdf, accessed Jan 17, 2020.

[78] Schober, Sugurd et al "A method for the determination of polyunsaturated fatty acid methyl esters in biodiesel: Results of an interlaboratory study," European Journal of Lipid Science and Technology, published online 8/26.09. Digital Abstract: http://onlinelibrary.wiley.com/doi/10.1002/ejlt.200800266/abstract, accessed Jan 17, 2020.

triglycerides.[79] This is another area recommended for future work. GC analysis could also be applied to the detection and identification of additives and adulterants in biodiesel.

Effective quality testing for a broad range of biodiesel blends utilizing approved ASTM methods has demonstrated promise for the expansion of these methods to support testing and commercial introduction of biodiesel blends from B20 to B100 from established feedstocks. The viability of additional feedstocks (jatropha, flaxseed, cottonseed, palm oil and coconut oil) should be evaluated along with the associated test methods as their market presence becomes more commonplace. The expansion of viable alternative feedstocks will also require additional test method research and development to support quality verification by both industry producers and public agencies.

Table 55: Summary of ASTM Test Method Results for Biodiesel Blends

ASTM Method	ASTM Method Title	Summary of Results
D2500-09	Standard Test Method for Cloud Point of Petroleum Products	Method works for all blend stocks at all levels
D4539-10	Standard Test Method for Filterability of Diesel Fuels by LTFT Test	Saff/Can and WCO A-66 were not tested because blend stocks were completely used in other testing. Method worked for the three blends tested for Soy, with a highly linear correlation. Method worked for the three blends tested for WCO A-67E, with a non-linear correlation. Method works for all blends tested; additional work is needed.
D6371-05	Standard Test Method for CFPP of Diesel and Heating Fuels	Method works for all blend stocks at all levels. Rough linear correlation for Soy and WCO blends. Biphasic response for Saff/Can blends.
D93-10a	Standard Test Method for Flash Point by Pensky-Martens Closed Cup Tester, Procedures A or C	Method works for all blend stocks at all levels. A non-linear response for all four feedstocks was observed.
D86-10a	Standard Test Method for Distillation of Petroleum Products At Atmospheric Pressure	Method did not work at or above B30 for any blend stock. Atmospheric Pressure Distillation is not applicable to biodiesel blends above B20.

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[79] De Jong, Rob and Rik Suijker, "GC Analysis of Biodiesels: Compliance with International Standards Using a Single System", American Laboratory October 2012. Reprinted online at http://www.paclp.com/content/documents/Press_Articles/ALM_October2012_web.pdf, accessed Jan 17, 2020.

ASTM Method	ASTM Method Title	Summary of Results
D1160-06	Standard Test Method for Distillation of Petroleum Products At Reduced Pressure	Method works for B90.and B100. Reduced Pressure Distillation by D1160-06 is not applicable to blends below B80.
D2709-96	Standard Test Method for Water and Sediment in Middle Distillate Fuels by Centrifuge	Method works for all blend stocks at all levels.
D7371-07	Standard Test Method for Determination of Biodiesel (Fatty Acid Methyl Esters) Content in Diesel Fuel Oil Using Mid Infrared Spectroscopy (FTIR-ATR-PLS Method)	Method works for all blend stocks at all levels.
D6584-10a	Standard Test Method for Determination of Total Monoglyceride, Total Diglyceride, Total Triglyceride, and Free and Total Glycerin in B-100 Biodiesel Methyl Esters by Gas Chromatography	Method works for all neat blend stocks. Method did not work for any blends because of interference from petroleum diesel components.
D445-10	Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)	Method works for all blend stocks at all levels. A linear correlation of kinematic viscosity with blend level observed for all blend stocks.

Source: ASTM International

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ASTM Standard Specification D7467-10, "Standard Specification for Diesel Fuel Oil, Biodiesel Blend (B6 to B20)," ASTM International, West Conshohocken, PA, 2010.

ASTM Standard Test Method D86-10a, "Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure," ASTM International, West Conshohocken, PA, 2010.

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GLOSSARY

ACCEPTANCE TOLERANCE—the accuracy tolerance applied to a weighing or measuring device during type evaluation or after installation or repair (see accuracy tolerance).

ACCURACY TOLERANCE—the acceptable error in the indicated delivery of a weighing or measuring device.

AMERICAN NATIONAL STANDARDS INSTITUTE (ANSI)—A private, not-for-profit organization created to support the U.S. voluntary standards and conformity assessment system.

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM)—An international standards organization that develops and publishes voluntary consensus technical standards for a wide range of materials, products, systems, and services. They provide accreditation for standards developed by other groups and individuals.[80]

ANALYTE—a chemical substance that is the subject of chemical analysis.[81]

ATMOSPHERIC EQUIVALENT TEMPERATURE (AET)—In atmospheric science, equivalent temperature is the temperature of an air parcel from which all the water vapor has been extracted by an adiabatic process.[82]

ATMOSPHERIC EQUIVALENT TEMPERATURE AT 90 PERCENT RECOVERY (AET_{90})— In the atmospheric distillation test method *D86-10a,* the temperature at which 90 volume percent of the sample is recovered is measured.

ATMOSPHERIC EQUIVALENT TEMPERATURE AT FINAL BOILING POINT (AET_f)—The average final AET temperature reported in degrees Celsius, with the corresponding volume percent recovered at a predetermined distillation stop point.

ATTENUATED TOTAL REFLECTANCE (ATR)—A sampling technique used in conjunction with infrared spectroscopy which enables samples to be examined directly in the solid or liquid state without further preparation.

BIODIESEL—a manufactured mixture of esters of glycerin with straight chain fatty acids obtained from plant or animal fats and oils.

BOILING POINT, FINAL AND INITIAL (FBP, IBP)—The temperature at which a component's vapor pressure equals atmospheric pressure. Boiling point is a relative indicator of volatility and generally increases with increasing molecular weight.

CALIFORNIA AIR RESOURCES BOARD (ARB)—The "clean air agency" in the government of California whose main goals include attaining and maintaining healthy air quality, protecting the public from exposure to toxic air contaminants, and providing innovative approaches for complying with air pollution rules and regulations.

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[80] American National Standards Institute (https://www.ansi.org/about_ansi/overview/overview)

[81] Merriam-Webster (https://www.merriam-webster.com/dictionary/analyte)

[82] Equivalent Temperature (https://en.wikipedia.org/wiki/Equivalent_temperature)

CALIFORNIA BUSINESS AND PROFESSIONS CODE (BPC)—One of the 29 codes enacted by California Law.[83]

CALIFORNIA CODE OF REGULATIONS (CCR)—The official compilation and publication of the regulations adopted, amended, or repealed by state agencies pursuant to the Administrative Procedure Act (APA). Properly adopted regulations that have been filed with the Secretary of State have the force of law. The CCR is compiled into Titles and organized into Divisions containing the regulations of state agencies.[84]

CALIFORNIA DEPARTMENT OF FOOD AND AGRICULTURE (CDFA)—A cabinet-level agency in the California government responsible for the regulation of food, protecting agriculture from pests, promoting California’s agricultural industry, and enforcing standards for most petroleum products.[85]

CALIFORNIA ENERGY COMMISSION (CEC)—The state agency established by the Warren-Alquist State Energy Resources Conservation and Development Act in 1974 (Public Resources Code, Sections 25000 et seq.) responsible for energy policy. The Energy Commission's five major areas of responsibilities are:

1. Forecasting future statewide energy needs
2. Licensing power plants sufficient to meet those needs
3. Promoting energy conservation and efficiency measures
4. Developing renewable and alternative energy resources, including providing assistance to develop clean transportation fuels
5. Planning for and directing state response to energy emergencies.

CALIFORNIA FUEL CELL PARTNERSHIP (CaFCP)—The California Fuel Cell Partnership is an industry/government collaboration aimed at expanding the market for fuel cell electric vehicles powered by hydrogen to help create a cleaner, more energy-diverse future with no-compromises to zero emission vehicles.

CARBON DIOXIDE ($CO2$)—A colorless, odorless, nonpoisonous gas that is a normal part of the air. Carbon dioxide is exhaled by humans and animals and is absorbed by green growing things and by the sea. CO2 is the greenhouse gas whose concentration is being most affected directly by human activities. CO2 also serves as the reference to compare all other greenhouse gases (see carbon dioxide equivalent).

CAVITY RING DOWN SPECTROMETRY (CRDS)—a highly sensitive laser absorption spectroscopy technique that is able to measure absolute absorption cross sections and has

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[83] California State Legislature (http://www.legislature.ca.gov/research_and_publications/laws_and_constitution/laws_and_constitution.html)

[84] California Office of Administrative Law (https://oal.ca.gov/)

[85] California Department of Food and Agriculture (https://www.cdfa.ca.gov/CDFA-Mission.html)

found wide applications in molecular spectroscopy. The exponential decay of laser intensity leaking from a high-finesse optical cavity is measured.[86]

CETANE NUMBER—a measure of the ignition delay of a diesel fuel in a compression ignition engine relative to cetane (n-hexadecane). In California, the ARB sets a minimum cetane number of 53 (CCR Section 2282(h)).

CLOUD POINT—the temperature at which waxy material begins to precipitate out from a diesel or biodiesel fuel. The cloud point is one measure of low temperature performance.

COLD FILTER PLUGGING POINT (CFPP)—A measure of cold flow properties useful for judging the low temperature performance of conventional diesel fuels.

COMPRESSION IGNITION ENGINE—an internal combustion engine using heat from the compression of the mixture of air and fuel in the cylinders to ignite the fuel.

COMPRESSED NATURAL GAS (CNG)—Natural gas that has been compressed under high pressure, typically between 2,000 and 3,600 pounds per square inch, held in a container. The gas expands when released for use as a fuel.

DIRECT CURRENT (DC)—A charge of electricity that flows in one direction and is the type of power that comes from a battery.

DIVISION OF MEASUREMENT STANDARDS (DMS)—Enforcer of California’s weights and measures laws and regulations. The DMS’s activities are designed to ensure the accuracy of commercial weighing and measuring devices; verify the quantity of both bulk and packaged commodities; and enforce the quality advertising, and labeling standards for most petroleum products.[87]

DISTILLATION– a method of separating the components of a mixture based on differences in vapor pressure by applying heat at a controlled rate.

EXAMINATION PROCEDURE OUTLINE (EPO)—A document used by the National Institute of Standards and Technology that is a written set of instructions laying out the procedure to use when evaluating a device.[88]

ENVIRONMENTAL PROTECTION AGENCY (EPA)—A federal agency created in 1970 to permit coordinated governmental action for protection of the environment by systematic abatement and control of pollution through integration or research, monitoring, standards setting and enforcement activities.

ESTER—an organic molecule formed by the condensation of a carboxylic acid with an organic alcohol.

FATTY ACID METHYL ESTERS (FAME)—A type of fatty acid ester that are derived by transesterification of fats with methanol. The molecules in biodiesel are primarily FAMEs,

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[86] University of Louisville (http://louisville.edu/faculty/j0liu028/research/cavity-ring-down-spectroscopy)

[87] California Department of Food and Agriculture (https://www.cdfa.ca.gov/dms/)

[88] National Institute of Standards and Technology (https://www.nist.gov/pml/weights-and-measures/publications)

usually obtained from vegetable oils by transesterification. They are used to produce detergents and biodiesel.

FLAME IONIZATION DETECTOR (FID)—Used to detect the presence of potentially flammable or toxic gases and vapors. FIDs are the most widely used detectors in gas chromatographic instruments for measuring hydrocarbons and other organic species.[89]

FLASH POINT—the lowest temperature at which there is a sufficient quantity of vapor formed to ignite under the conditions specified in ASTM *D93-10a*.

FOURIER TRANSFORM-INFRARED SPECTROSCOPY (FTIR)—An analytical technique used to identify organic (and in some cases inorganic) materials. This technique measures the absorption of infrared radiation by the sample material versus wavelength.

FUEL CELL ELECTRIC VEHICLE (FCEV)—A zero-emission vehicle that runs on compressed hydrogen fed into a fuel cell "stack" that produces electricity to power the vehicle.

GAS CHROMATOGRAPHY-ELECTRON CAPTURE DETECTOR (GC-ECD, ECD)—a device for detecting atoms and molecules in a gas through the attachment of electrons via electron capture ionization.[90]

GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS, MS)—An analytical technique used to separate, identify, and quantify chemical mixtures. It combines the features of gas-chromatography and mass spectrometry.[91]

GAS CHROMATOGRAPHY-PULSED DISCHARGE HELIUM IONIZATION DETECTOR (GC-PDHID, PDHID)—A detector for gas chromatography that utilizes a stable, low powered, pulsed DC discharge in helium as an ionization source.[92]

GAS CHROMATIOGRAPHY-PULSED FLAME PHOTOMETRIC DETECTOR (GC-PFPD, PFPD)—An updated version of flame-based gas chromatographic detectors. It operates in a pulsed-flame mode rather than continuous-flame mode.

GAS CHROMATOGRAPHY-THERMAL CONDUCTIVITY DETECTOR (GC-TCD, TCD)—A technique used to analyze inorganic gases and small hydrocarbon molecules. The TCD compares the thermal conductivity of two gas flows – the pure carrier (reference) gas and the sample. Changes in the temperature of the electrically-heated wires in the detector are affected by the

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[89] U.S. Department of Homeland Security (https://www.dhs.gov/sites/default/files/publications/FID-PID-MSR_0415-508.pdf)

[90] Air Products Analytical Laboratories (https://www.airproducts.com/industries/Analytical-Laboratories/analytical-lab-applications/product-list/gc-with-electron-capture-detector-gc-ecd-analytical-laboratories.aspx?itemId=2ED69212C574443C9354860ABEFCFE2B)

[91] American Chemical Society (https://www.acs.org/content/acs/en/education/whatischemistry/landmarks/gas-chromatography-mass-spectrometry.html)

[92] Chromatographia Information (https://link.springer.com/article/10.1007/BF02268349)

thermal conductivity of the gas which flows around this. The changes in this thermal conductivity are sensed as a change in electrical resistance and are measured.[93]

GREENHOUSE GAS (GHG)—Any gas that absorbs infrared radiation in the atmosphere. Greenhouse gases include water vapor, carbon dioxide (CO2), methane (CH4), nitrous oxide (NOx), halogenated fluorocarbons (HCFCs), ozone (O3), perfluorinated carbons (PFCs), and hydrofluorocarbons (HFCs).

HYDROGEN FIELD STANDARD (HFS)—A physical reference standard created in order to test the accuracy of hydrogen dispensers. The major components of the HFS are the three working standards (gravimetric, volumetric, and master meter), a programmable logic controller, data acquisition and display electronics, two hydrogen fill tanks, piping and valves connecting the tanks, standards, and hydrogen source, and a supporting framework for mounting and transport.

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION (ISO)—An independent, non-governmental organization with members from standards organizations in 164 member countries. It is the world's largest developer of voluntary international standards and facilitates world trade by providing common standards between nations.[94]

INTERNATIONAL SYSTEM OF UNITS (SI)—French Système Internationale d’Unités, international decimal system of weights and measures derived from and extending the metric system of units. Adopted by the 11th General Conference on Weights and Measures in 1960, it is abbreviated SI in all languages.[95]

ION CHROMATOGRAPHY (IC)—A form of liquid chromatography that measures concentrations of ionic species by separating them based on their interaction with a resin.[96]

KINEMATIC VISCOSITY—a measure of the resistance to flow of a liquid taking its density into account. Vehicle engines are designed to operate with fuel in a specified range of viscosity.

LEGAL METROLOGY—the regulatory framework governing the application of metrology to commercial transactions to ensure the accuracy of commercial measurements, enhance consumer protection, foster competition, and facilitate state and national economic growth and trade.

LOW-TEMPERATURE FLOW TEST (LTFT) —A test used to estimate the filterability of a fuel in diesel equipment.

METHOD DETECTION LIMIT—The minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater

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[93] Air Products Analytical Laboratories (https://www.airproducts.com/industries/Analytical-Laboratories/analytical-lab-applications/product-list/gc-with-thermal-conductivity-detector-gc-tcd-analytical-laboratories.aspx?itemId=651A80DACEBF49F4993E7C447B42808E)

[94] International Organization for Standardization (https://www.iso.org/about-us.html)

[95] Encyclopedia Britannica (https://www.britannica.com/science/International-System-of-Units)

[96] Microbial Life Educational Resources (https://serc.carleton.edu/microbelife/research_methods/biogeochemical/ic.html)

than zero and is determined from analysis of a sample in a given matrix containing the analyte.[97]

NATIONAL CONFERENCE ON WEIGHTS AND MEASURES (NCWM)—A professional association of state and local weights and measures officials, federal agencies, manufacturers, retailers and consumers. NCWM has developed national weights and measures standards since 1905.[98]

NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY (NIST)—A non-regulatory agency created to promote U.S. innovation and industrial competitiveness by advancing measurement science, standards, and technology in ways that enhance economic security and improve quality of life.[99]

NATIONAL RENEWABLE ENERGY LABORATORY (NREL)—The United States' primary laboratory for renewable energy and energy efficiency research and development. NREL is the only Federal laboratory dedicated to the research, development, commercialization, and deployment of renewable energy and energy efficiency technologies. Located in Golden, Colorado.

NATIONAL TYPE EVALUATION PROGRAM (NTEP)—The NTEP program is administered through the National Conference on Weights and Measures (NCWM). NTEP requires industry to submit prototype weighing devices for evaluation to determine whether or not it meets the uncertainties which are related to tolerances associated with the intended final use in the marketplace.[100]

NITROGEN OXIDES (NOx)—A general term pertaining to compounds of nitric oxide (NO), nitrogen dioxide (NO2), and other oxides of nitrogen. Nitrogen oxides are typically created during combustion processes and are major contributors to smog formation and acid deposition. NO2 is a criteria air pollutant and may result in numerous adverse health effects.

NO. 1 DIESEL—A middle-distillate petroleum diesel fuel with a T90 equal to 550 °F and meeting the specifications of ASTM *D975-10c*.

NO. 2 DIESEL—A middle-distillate petroleum diesel fuel with a T90 equal to 640 °F and meeting the specifications of ASTM *D975-10c*.

ORIGINAL EQUIPMENT MANUFACTURER (OEM)—Here, refers to engine and/or automobile manufacturers.

PARTS PER BILLION (ppb)—Measurement of quantity.

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[97] U.S. EPA System of Registries Glossary (https://ofmpub.epa.gov/sor_internet/registry/termreg/searchandretrieve/glossariesandkeywordlists/search.do?details=&vocabName=NPDES%20Glossary#formTop)

[98] National Association of State Departments of Agriculture (https://www.nasda.org/organizations/national-conference-on-weights-and-measures-ncwm)

[99] USAGov National Institute of Standards and Technology (https://www.usa.gov/federal-agencies/national-institute-of-standards-and-technology)

[100] National Institute of Standards and Technology (https://www.nist.gov/programs-projects/national-type-evaluation-program-ntep)

POUNDS PER SQUARE INCH (PSI)—A unit of pressure or stress based on avoirdupois units. It is the pressure resulting from a force of one pound-force applied to an area of one square inch.

PRESSURE-VOLUME-TEMPERATURE STANDARD (PVT): Hydrogen gas is dispensed into tanks similar to those installed in fuel cell vehicles. The density of the gas in the tank is calculated from pressure and temperature measurements on the gas using the NIST equation of state values. By multiplying the density by the tank's known internal volume, the mass of hydrogen dispensed into the field reference standard can be calculated.

SAE INTERNATIONAL (SAE)—A global association of more than 128,000 engineers and related technical experts in the aerospace, automotive, and commercial-vehicle industries. The leader in connecting and educating mobility professionals to enable safe, clean, and accessible mobility solutions, known as Society of Automotive Engineers until 2006.[101]

SAFFLOWER/CANOLA OIL BLEND STOCK (Saff/Can)—An oil blend stock used in this study.

TOTAL HYDROCARBON (THC)—Total hydrocarbon emissions that also serve as a surrogate for the emissions of organic hazardous air pollutant compounds.

UNITED STATES DEPARTMENT OF ENERGY (DOE)—The federal department established by the Department of Energy Organization Act to consolidate the major federal energy functions into one cabinet-level department that would formulate a comprehensive, balanced national energy policy. DOE's main headquarters are in Washington, D.C.

U.S. NATIONAL WORK GROUP (USNWG)—works to promote, encourage, and participate in the establishment of a comprehensive set of legal metrology standards for commercial measurement of hydrogen for vehicle and other refueling applications including (1) device design, accuracy, installation, and use requirements; (2) method of sale requirements; (3) test procedures; and (4) fuel quality standards. The ultimate goal is that these standards will ensure the accuracy of measurements, enhance consumer protection, foster fair competition, and facilitate economic growth and trade.[102]

WASTE COOKING OIL (WCO)—Second-hand cooking oil that can be used to produce biodiesel.[103]

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[101] Society of Automotive Engineers (https://www.sae.org/about/)

[102] National Institute of Standards and Technology (https://www.nist.gov/pml/weights-and-measures/legal-metrology-devices/hydrogen-us-national-work-group)

[103] Alternative Fuels Data Center (https://afdc.energy.gov/glossary.html#W)

Appendix A: Timeline for Fuel Cell Vehicles and California's Hydrogen Infrastructure

1931 – The California Legislature enacted the Oil Substitution Act (Stats 1931, Chapter 609). This Act sought to prevent fraud in the sale of transportation fuels in California and to ensure that all fuels sold met accepted quality standards. The DMS of the CDFA was given the responsibility for establishing and enforcing the quality standards for transportation fuels sold in California. Products are sampled and tested in the CDFA's laboratories in Sacramento and Anaheim to verify that they meet the quality, performance and drivability standards established in state law.

1949 - California Agricultural Act - Chapter 893 §2 was amended to require the CDFA to develop regulations for the testing of types or designs of weights, measures, and weighing and measuring devices (type testing) used for commercial purposes. This amendment gave the CDFA the authority to regulate transportation fuel dispensers in California.

1989 - The National Hydrogen Association (NHA) was formed in the United States with ten members. Today, the NHA has nearly 100 members, including representatives from the automobile and aerospace industries, all levels of government, universities, researchers, utilities, and energy providers. The International Organization for Standardization's Technical Committee for Hydrogen Technologies was also created in 1989.

1990 – The ARB introduced the Zero Emission Vehicle (ZEV) Mandate. The mandate was the first public policy aimed at the improvement of air quality through new technologies instead of modifications of the internal combustion engine.

1999 – The California Fuel Cell Partnership is formed, bringing the ARB and CEC together with DaimlerChrysler, the Ford Motor Company, Ballard Power Systems, BP, Shell Hydrogen, and ChevronTexaco to promote fuel cell vehicle development. The following year, the Partnership's headquarters opened in West Sacramento, California.

2001 – The first 10,000 psi hydrogen tanks were demonstrated, increasing the driving range of fuel cell vehicles while decreasing the size of on-board storage tanks.

2003 - President Bush announced the Hydrogen Fuel Initiative, a $1.2 billion federal program to fund hydrogen technology development.

2003 – The CEC issued the *2003 Integrated Energy Policy Report,* calling for a reduction in petroleum fuel use in the transportation sector to 15 percent below 2003 levels by 2020, and an increase in the use of nonpetroleum fuels to 20 percent of on-road fuel consumption by 2020 and 30 percent by 2030.[104]

2004 - California Governor Arnold Schwarzenegger signs Executive Order S-7-04, committing the state to the development of the California Hydrogen Highway. The goals of this ambitious plan are yet to be fully realized. However, this order established California as a national leader in the development of a hydrogen economy.

2005 – AB 1007 (Pavley) calls for the development of a program to promote alternative fuels and vehicle technologies in California to reduce petroleum dependence and improve air quality.

2007 - Assembly Bill 118 (Núñez) created the CEC's Alternative and Renewable Fuel and Vehicle Technology Program. The statute, subsequently amended by Assembly Bill 109 (Núñez, Chapter 313, Statutes of 2008), authorized the CEC to develop and deploy alternative and renewable fuels and advanced transportation technologies to help attain the state's climate change and clean air policies.

2007 - The U.S. National Work Group (USNWG) for the Development of Hydrogen Measurement Standards was established in October of 2007 to assist stakeholders in promoting the legal use of hydrogen dispensers for fuel cell vehicles in commerce.

2007 – General Motors launched Project Driveway to put 100 Chevy Equinox Fuel Cell SUVs on the road in Los Angeles, Orange County, New York, and Washington DC as part of GM's fuel cell research program.

2009 – The annual Investment Plan for AB 118 provided $3.5 million for the DMS of the CDFA to research hydrogen fuel dispensing device test standards and procedures, fuel sampling techniques and laboratory methods for hydrogen fuel quality analysis.

2012 – California Governor Jerry Brown signs Executive Order 16-2012, setting goals to increase the number of Zero Emission Vehicles on the State's highways and to develop the infrastructure needed to support them.

2013 – The H_2USA public-private partnership is established under the sponsorship of the U. S. Department of Energy to promote the development of hydrogen infrastructure.

2015-2017 – Major automobile manufacturers plan to offer fuel cell vehicles for sale in California.

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[104] California Energy Commission *2003 Integrated Energy Policy Report*: www.energy.ca.gov/reports/100-03-019F.PDF, accessed June 14, 2013.

Appendix B: Preparation of Standards for Hydrogen Analysis

Procedure: Excel spreadsheets and logbooks are used to maintain traceability of all standards and solutions prepared. All standards and solutions prepared are recorded in the *Sacramento Hydrogen Standards Logbook*'. An Excel template may be used to determine the volumes of standards required for the desired concentration of standard. Standard mixtures are numbered sequentially using the format SHS-XXX, where SHS stands for Sacramento Hydrogen Standard, and XXX is the next number.

Determination of Standards volumes to use: Most of the standards prepared will be in the low to mid-ppm range. The volumes of analyte that are necessary can be calculated using the 'Standard Prep Template'. A sample template is shown below in Figure 57. When the 'Desired Final Conc' and 'Desired Final Pressure' are entered in the template, the volume needed is automatically calculated.

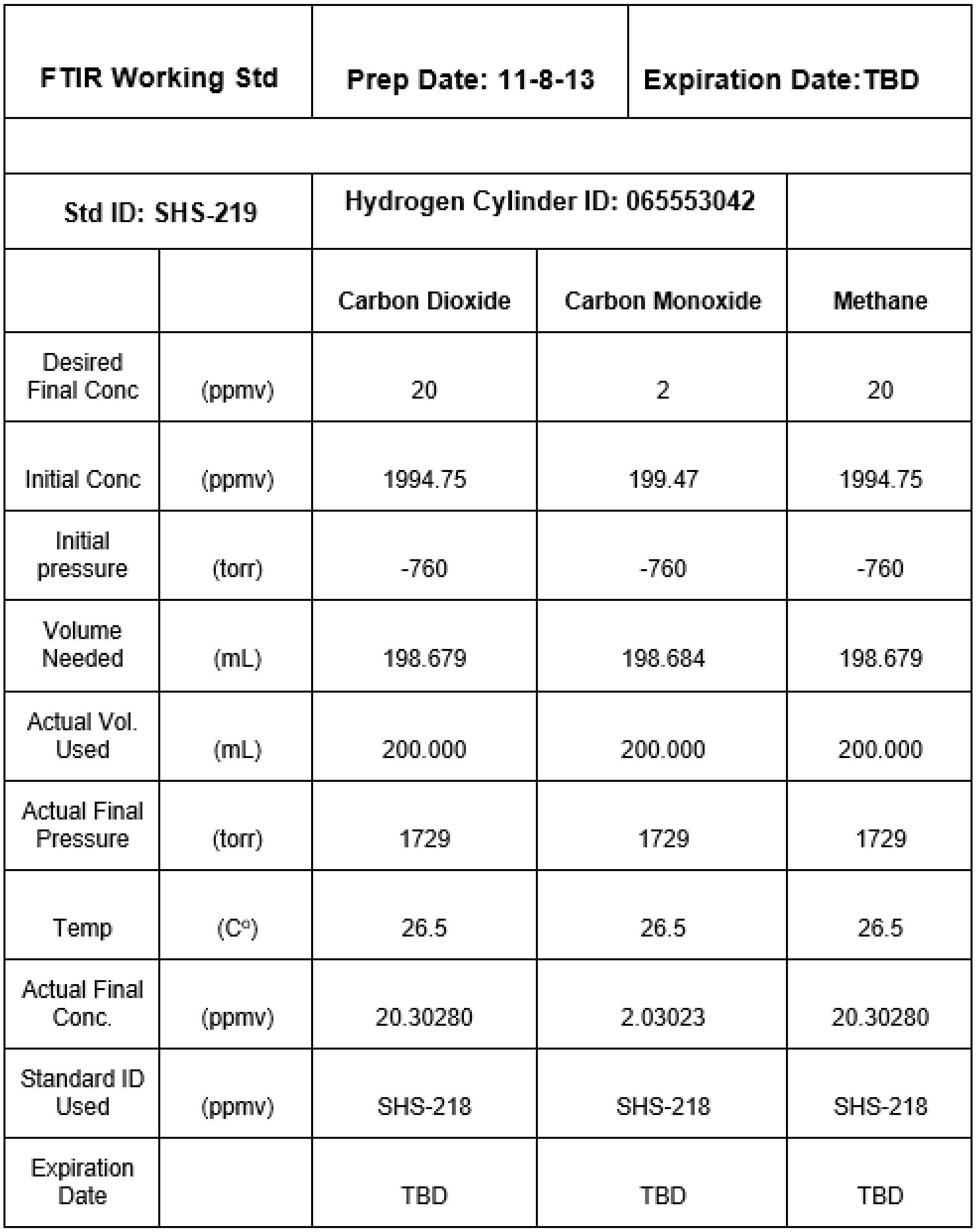
The volume of neat material that will be required depends on the final container; this will probably be 6 L, but other size containers can be used. The final pressure can be adjusted to obtain manageable volumes. For example, the final pressure can be adjusted to give a volume needed of 120.0 ml rather than 117.63 ml. **Note: for safety reasons, the final pressure in the SUMMA cans must not exceed 40 psig; this is a final gauge pressure of 2080 Torr.** It should also be noted that pressurizing the canister towards the maximum pressure will give more standard that can be used since standards flow out of the canister by pressure and are not evacuated by vacuum. A typical CCV analysis on the FTIR may use > 3 L. A standard canister that contains more will last longer.

Most of the analytes that must be prepared are in the gaseous phase, a few will be in the liquid phase. Most liquid analytes will require the preparation of an intermediate, high level parent (or parent mixture). To calculate the volume of liquid standard to be used, the spreadsheet must be modified in the 'Volume needed' column, to account for the molecular weight of the compound.

Canister preparation: First, obtain a clean 6 L SUMMA canister; one that immediately prior held the same mixture is preferred, as potential active sites within the canister are minimized. Ensure the valve on the canister is closed, remove the brass cap and attach the canister snugly to the bottom of the pressurization station. Familiarize yourself with the use of the gauge prior to attempting to prepare standards. Also note that the gauge is a combination vacuum / pressure gauge; it will read 0 T @ STP, and -760 T at full vacuum (0 T). This means it has a bias of 760 T, which is accounted for in the calculations.

Fill and evacuate the pressurization station 8-10 times using ultra high purity hydrogen. The canister is now ready for the standard. The following steps must all occur within the fume hood. Select the first analyte to be added. Using the gas-tight syringe that will be used to measure out the concentrated analyte, insert it through the septa. Then carefully back off the plunger to draw an aliquot of standard into the syringe, remove the syringe, and allow it to vent to room pressure. Quickly adjust the volume to the sample size needed and introduce the syringe into the septa in the pressurization station. The syringe should automatically expel its aliquot into the SUMMA canister; if does not, depress the plunger. Remove the syringe as soon as it is empty.

Figure B-1: Sample Spreadsheet for Standard Mixture Preparation



FTIR Working Std		**Prep Date: 11-8-13**	**Expiration Date:TBD**	
Std ID: SHS-219		**Hydrogen Cylinder ID: 065553042**		
		Carbon Dioxide	Carbon Monoxide	Methane
Desired Final Conc	(ppmv)	20	2	20
Initial Conc	(ppmv)	1994.75	199.47	1994.75
Initial pressure	(torr)	-760	-760	-760
Volume Needed	(mL)	198.679	198.684	198.679
Actual Vol. Used	(mL)	200.000	200.000	200.000
Actual Final Pressure	(torr)	1729	1729	1729
Temp	(C°)	26.5	26.5	26.5
Actual Final Conc.	(ppmv)	20.30280	2.03023	20.30280
Standard ID Used	(ppmv)	SHS-218	SHS-218	SHS-218
Expiration Date		TBD	TBD	TBD

Source: DMS Hydrogen Laboratory

Repeat this procedure for each analyte that is needed. When the final analyte has been added, pressurize the SUMMA canister to the desired final pressure. Allow the canister to thermal equilibrate for 12-15 minutes, and then bring the pressure up to the desired final pressure. It is almost impossible to exactly hit the desired final pressure, so record the actual final pressure and volumes used into the standard prep spreadsheet.

Print the spreadsheet out and tape the spreadsheet into the logbook, and sign and date across the tape. Print out a second copy of the spreadsheet, place it into a transparent job folder, and zip-tie it to the canister.

The specifications for impurities in fuel cell grade Hydrogen are in ppm v/v (parts per million volume-to-volume). This means a 100 ppm specification is equal to 100 mL in 1,000,000 ml. This is in contrast to more familiar units such as ug/L or ng/ml. The conversion can however easily be done; A conversion can be based on the fact that 1 mole of any gas occupies a volume of 22,400 mL at 0_o C and 760 T. A calculation for a 100 ppm Argon standard is shown.

100 mL Ar /10_6 mL H_2 x 40 g Ar /22,400 mL Ar x 10_6 ug Ar /1 g Ar =

0.1785 ug Ar/ mL H_2 @STP

Appendix C: Procedure for Cleaning Sampling and Standard Containers

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Summary of DMS Hydrogen Laboratory Procedure for Evacuation and Cleaning of Sampling and Standard Containers.

Scope: To cover the procedures necessary to ensure that sampling containers are clean prior to being placed into service, and are cleaned between uses, in order to prevent cross-contamination.

Reason: Detectable amounts of analytes may be present in sample containers and standard canisters in subsequent analyses of standard and sample bombs if high level contaminants (above the Maximum Contaminant Level, MCL) were present in the container immediately prior to use. To ensure sample and standard integrity, all containers must be cleaned following this SOP. All standards and sample containers are cleaned using the Entech canister cleaning system shown in Figure 58. The system consists of two ovens, vacuum pumps and control module, and operating software. The use of two ovens allows standard canisters and sample containers to be cleaned separately. This minimizes the chances of cross-contamination.

Figure C-1: Canister Cleaning System

Source: DMS Hydrogen Laboratory

Procedure:

1. Turn on the ovens. Start the Entech software and choose 'Close all valves'.
2. Record the Container ID#, Sample ID#, and date in the Canister Cleaning Log.
3. Vent all standard canisters and sample containers to atmospheric pressure inside the hood.
4. Attach 6 L SUMMA canisters to the manifold in the left-hand oven. The oven will hold up to eight canisters. Attach brass plugs to any manifold legs not used. Figure 59 shows two canisters mounted in the cleaning oven.

Figure C-2: SUMMA Canisters in the Cleaning Oven

Source: DMS Hydrogen Laboratory

5. For sample containers, place a brass cap on one of the two valves, and attach the other end to one of the brass lines in the right-hand oven. The oven can hold up to four cylinders. Attach brass plugs to any manifold legs not used. Figure 60 shows two canisters mounted in the cleaning oven.
6. Turn on the rough pump. Monitor the system pressure on the computer; it should drop to zero within 5 minutes. If it does not, there is a leak that must be fixed before proceeding.
7. When the system is leak tight, open all valves on all containers, and monitor the pressure and vacuum again for 5 min. The pressure should drop to zero and hold there.
8. Run the software program. This program will automatically heat, pressurize the vessels with ultra high purity hydrogen, and evacuate them 10 times.
9. When all cycles have been completed, close all valves using the software program.

Figure C-3: Sample Containers in the Cleaning Oven

Source: DMS Hydrogen Laboratory

10. The canisters and containers are held under vacuum in the ovens until they are needed. Close all container valves prior to removing from the manifold. Record the date removed in the Canister Cleaning logbook.

Appendix D: Instrument Parameters for Hydrogen Fuel Quality Analysis

Table D-1: System 1

GC/MS system	Single quadrupole, Electron impact
GC/MS scan range	16-250 Da
Column ramp ($_o$C)	-40/15 – 3 -100/0 – 9 -200/5
Injection Cryo-traps ($_o$C)	-180
Sample Lines ($_o$C)	65
PFPD Temp / Gate delay/ Width	200 $_o$C / 6 ms / 10 ms
ECD Temp / range	250 $_o$C / 10

Source: DMS Hydrogen Laboratory

Table D-2: System 2

Sample line temperature ($_o$C)	65
Column temperature ($_o$C)	Isothermal @ 50
TCD / Filament temperatures ($_o$C)	100 / 250
PDHID temperature ($_o$C)	100
FID / Methanizer temperatures ($_o$C)	120 / 380

Source: DMS Hydrogen Laboratory

Table D-3: FTIR

Scan Range	4000 – 650 cm^{-1}
Scan # / Resolution	128 scans / 0.25 cm^{-1}
Gas Cell / Cell Windows	10 m Multi-pass / ZnSe windows
Gas Cell Temperature	110 ^{0}C
Detector	Liquid nitrogen cooled mercury cadmium telluride-A
Sample introduction	Temperature controlled @ 60 ^{0}C, 1/8” Silonite coated stainless steel tubing, Silonite coated switching valve.

Source: DMS Hydrogen Laboratory

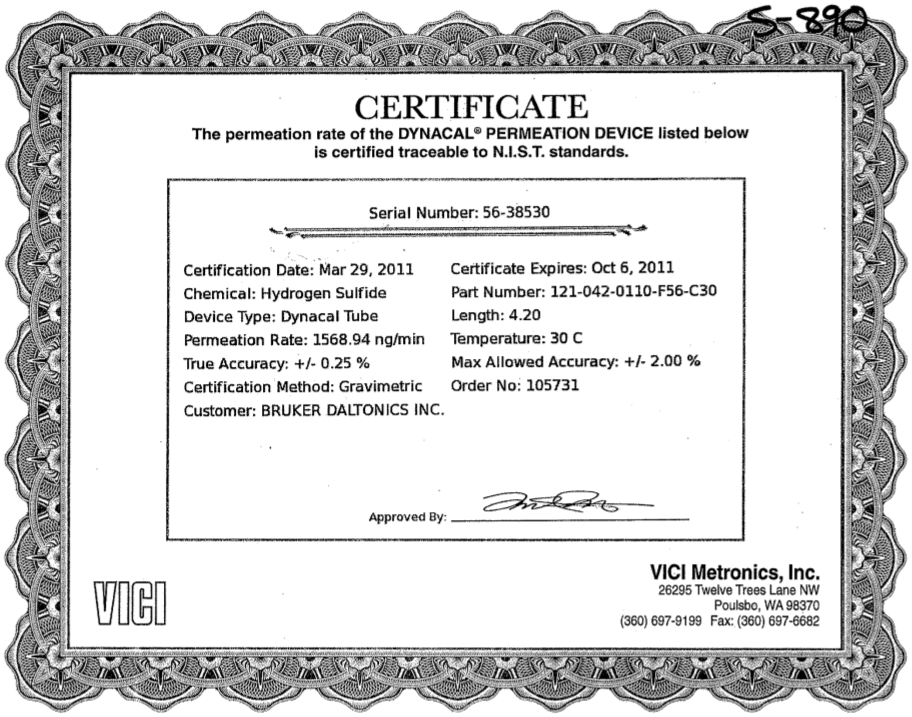
Table D-4: CRDS

Flow Rate	250-1000 mL/min
Purge Gas	Regulated ultra high purity H_2, purified, dried
Flow path	Parallel

Source: DMS Hydrogen Laboratory

Appendix E: Traceability Certificates

Figure E-1: Certificates for Dynacal Sulfur Permeation Tubes



S-890

CERTIFICATE

The permeation rate of the DYNACAL® PERMEATION DEVICE listed below is certified traceable to N.I.S.T. standards.

Serial Number: 56-38530

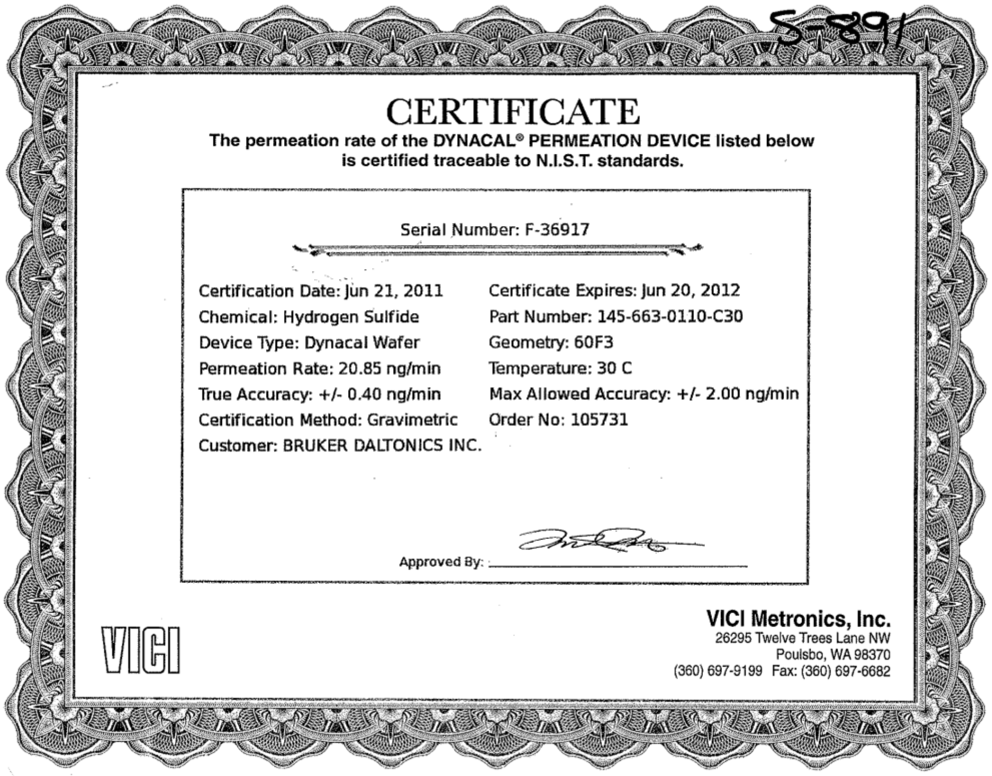
Certification Date: Mar 29, 2011
Chemical: Hydrogen Sulfide
Device Type: Dynacal Tube
Permeation Rate: 1568.94 ng/min
True Accuracy: +/- 0.25 %
Certification Method: Gravimetric
Customer: BRUKER DALTONICS INC.

Certificate Expires: Oct 6, 2011
Part Number: 121-042-0110-F56-C30
Length: 4.20
Temperature: 30 C
Max Allowed Accuracy: +/- 2.00 %
Order No: 105731

Approved By:

VICI

VICI Metronics, Inc.
26295 Twelve Trees Lane NW
Poulsbo, WA 98370
(360) 697-9199 Fax: (360) 697-6682



S-891

CERTIFICATE

The permeation rate of the DYNACAL® PERMEATION DEVICE listed below is certified traceable to N.I.S.T. standards.

Serial Number: F-36917

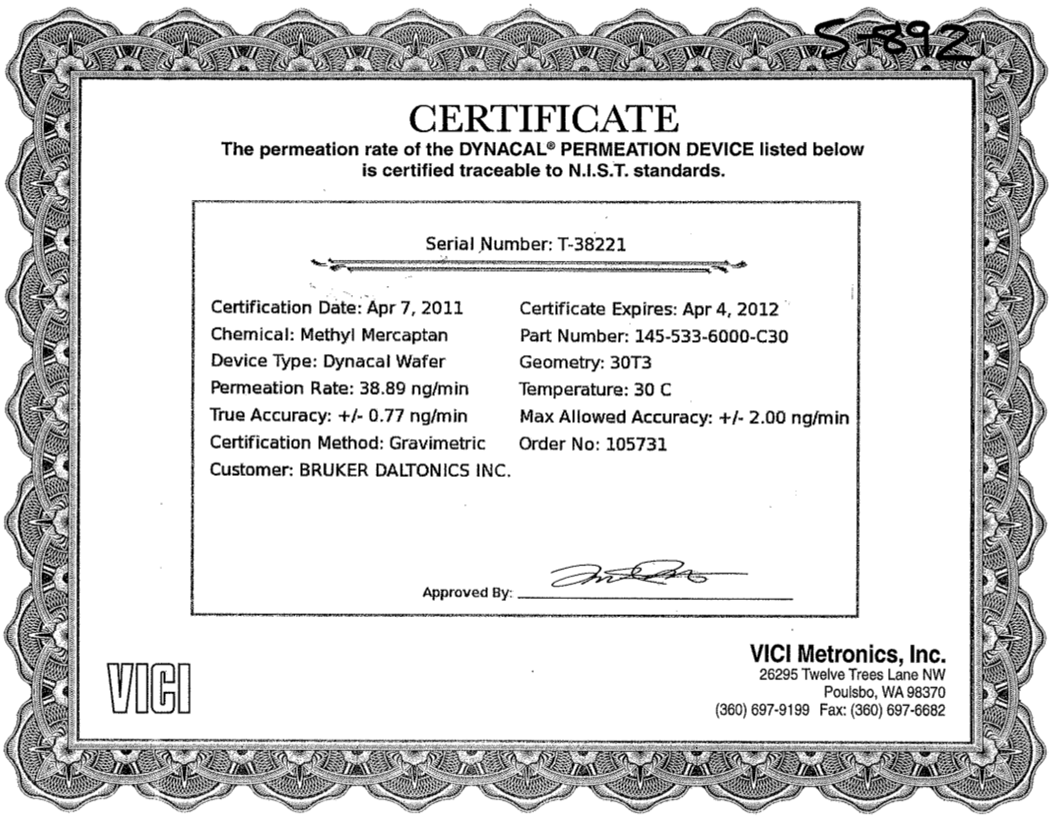
Certification Date: Jun 21, 2011
Chemical: Hydrogen Sulfide
Device Type: Dynacal Wafer
Permeation Rate: 20.85 ng/min
True Accuracy: +/- 0.40 ng/min
Certification Method: Gravimetric
Customer: BRUKER DALTONICS INC.

Certificate Expires: Jun 20, 2012
Part Number: 145-663-0110-C30
Geometry: 60F3
Temperature: 30 C
Max Allowed Accuracy: +/- 2.00 ng/min
Order No: 105731

Approved By:

VICI

VICI Metronics, Inc.
26295 Twelve Trees Lane NW
Poulsbo, WA 98370
(360) 697-9199 Fax: (360) 697-6682



S-892

CERTIFICATE

The permeation rate of the DYNACAL® PERMEATION DEVICE listed below is certified traceable to N.I.S.T. standards.

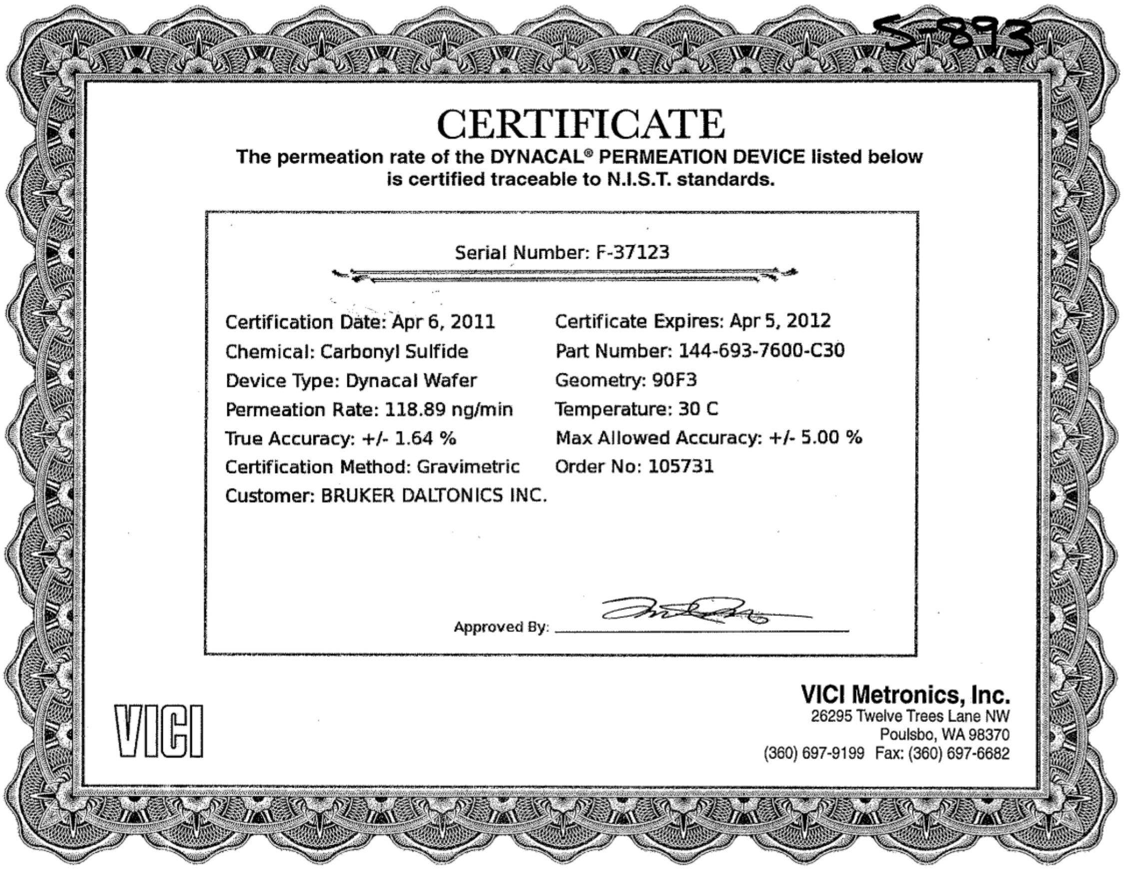
Serial Number: T-38221

Certification Date: Apr 7, 2011	Certificate Expires: Apr 4, 2012
Chemical: Methyl Mercaptan	Part Number: 145-533-6000-C30
Device Type: Dynacal Wafer	Geometry: 30T3
Permeation Rate: 38.89 ng/min	Temperature: 30 C
True Accuracy: +/- 0.77 ng/min	Max Allowed Accuracy: +/- 2.00 ng/min
Certification Method: Gravimetric	Order No: 105731
Customer: BRUKER DALTONICS INC.	

Approved By:

VICI

VICI Metronics, Inc.
26295 Twelve Trees Lane NW
Poulsbo, WA 98370
(360) 697-9199 Fax: (360) 697-6682



S-893

CERTIFICATE

The permeation rate of the DYNACAL® PERMEATION DEVICE listed below is certified traceable to N.I.S.T. standards.

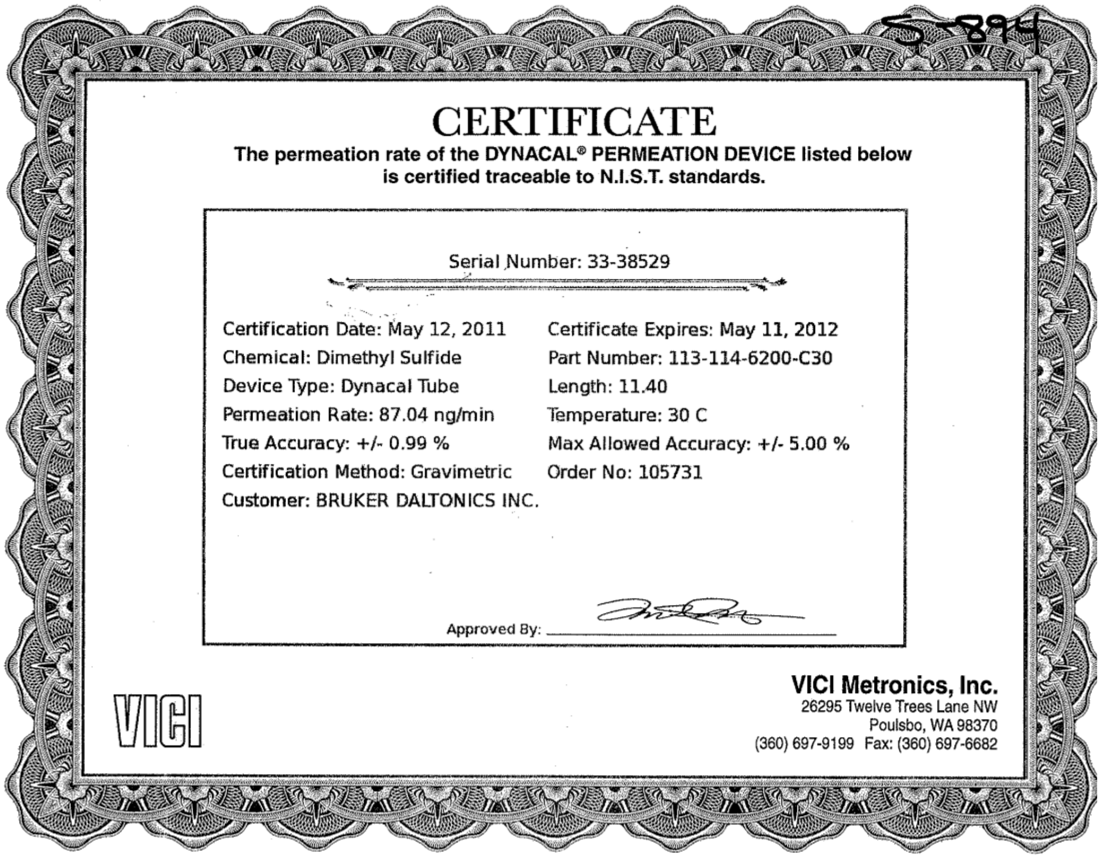
Serial Number: F-37123

Certification Date: Apr 6, 2011	Certificate Expires: Apr 5, 2012
Chemical: Carbonyl Sulfide	Part Number: 144-693-7600-C30
Device Type: Dynacal Wafer	Geometry: 90F3
Permeation Rate: 118.89 ng/min	Temperature: 30 C
True Accuracy: +/- 1.64 %	Max Allowed Accuracy: +/- 5.00 %
Certification Method: Gravimetric	Order No: 105731
Customer: BRUKER DALTONICS INC.	

Approved By:

VICI

VICI Metronics, Inc.
26295 Twelve Trees Lane NW
Poulsbo, WA 98370
(360) 697-9199 Fax: (360) 697-6682



S-894

CERTIFICATE

The permeation rate of the DYNACAL® PERMEATION DEVICE listed below is certified traceable to N.I.S.T. standards.

Serial Number: 33-38529

Certification Date: May 12, 2011	Certificate Expires: May 11, 2012
Chemical: Dimethyl Sulfide	Part Number: 113-114-6200-C30
Device Type: Dynacal Tube	Length: 11.40
Permeation Rate: 87.04 ng/min	Temperature: 30 C
True Accuracy: +/- 0.99 %	Max Allowed Accuracy: +/- 5.00 %
Certification Method: Gravimetric	Order No: 105731
Customer: BRUKER DALTONICS INC.	

Approved By: ____________________

VICI

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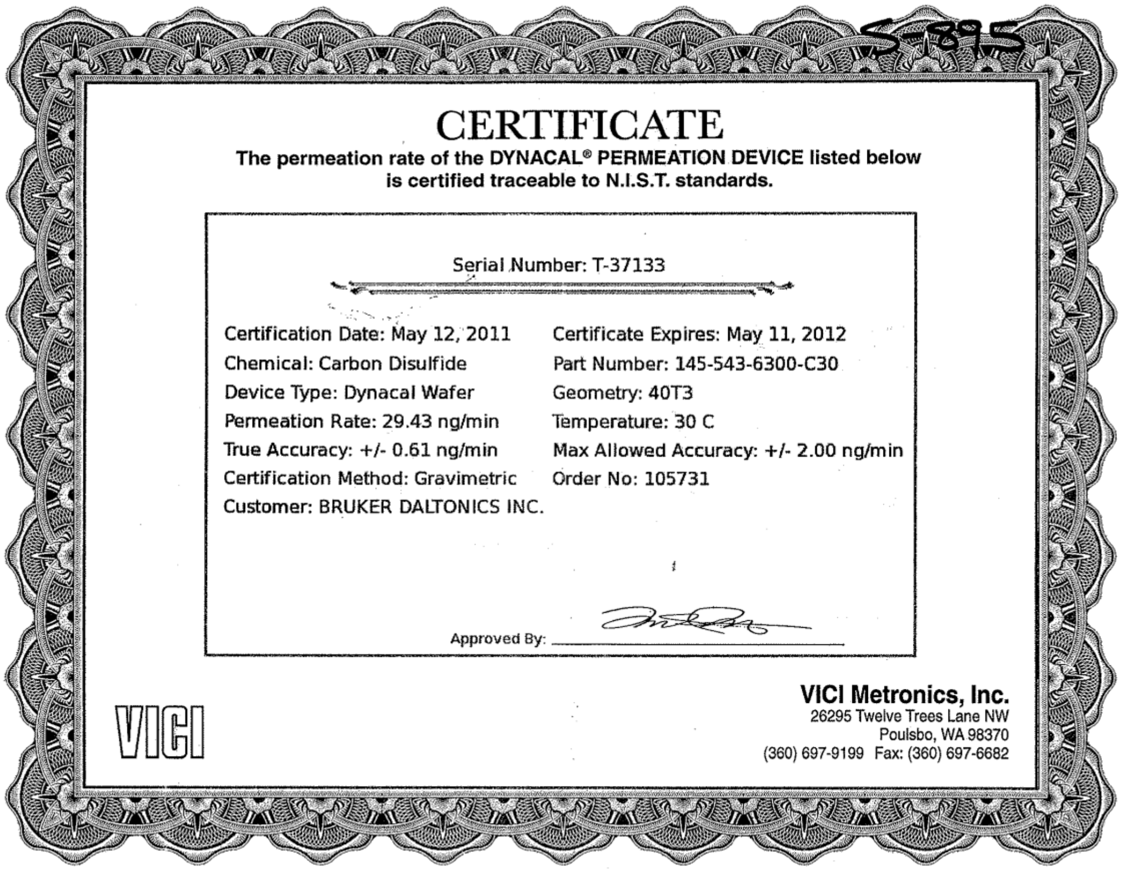
26295 Twelve Trees Lane NW
Poulsbo, WA 98370
(360) 697-9199 Fax: (360) 697-6682



S-895

CERTIFICATE

The permeation rate of the DYNACAL® PERMEATION DEVICE listed below is certified traceable to N.I.S.T. standards.

Serial Number: T-37133

Certification Date: May 12, 2011	Certificate Expires: May 11, 2012
Chemical: Carbon Disulfide	Part Number: 145-543-6300-C30
Device Type: Dynacal Wafer	Geometry: 40T3
Permeation Rate: 29.43 ng/min	Temperature: 30 C
True Accuracy: +/- 0.61 ng/min	Max Allowed Accuracy: +/- 2.00 ng/min
Certification Method: Gravimetric	Order No: 105731
Customer: BRUKER DALTONICS INC.	

Approved By: ____________________

VICI

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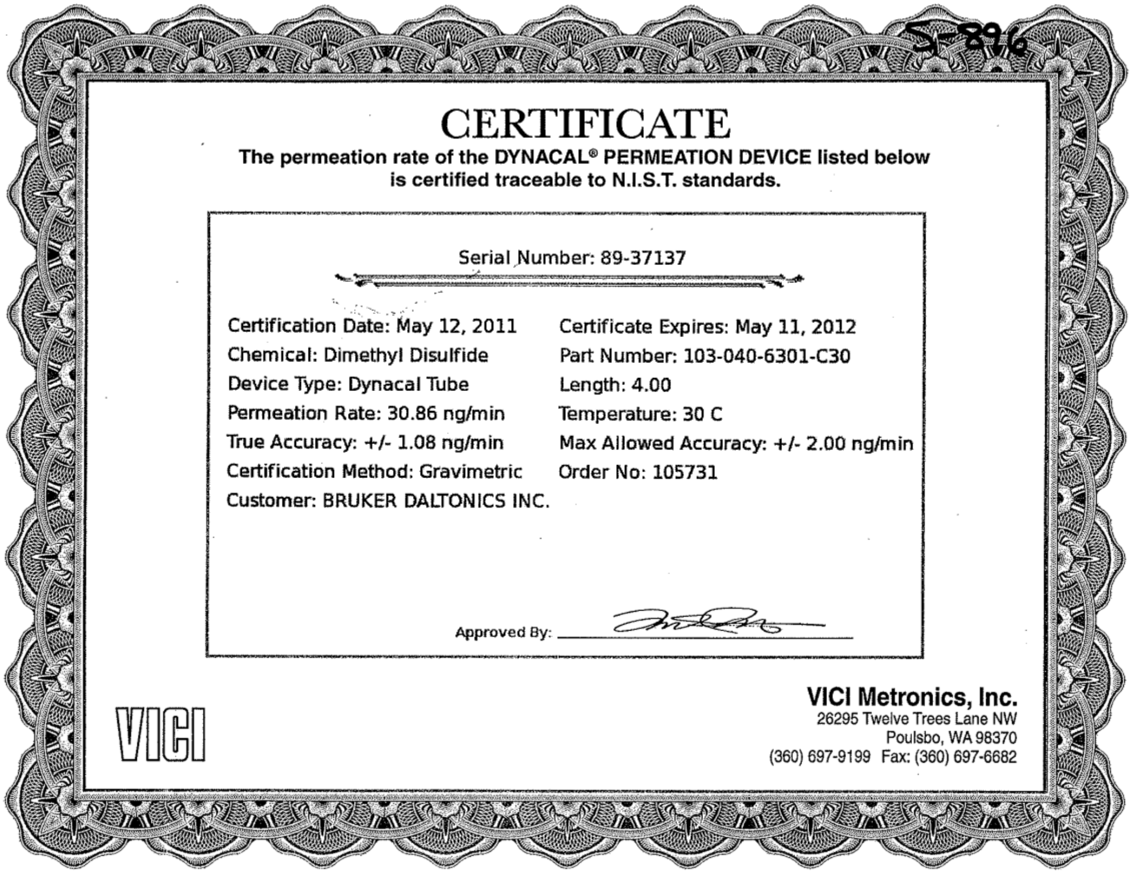
26295 Twelve Trees Lane NW
Poulsbo, WA 98370
(360) 697-9199 Fax: (360) 697-6682



S-896

CERTIFICATE

The permeation rate of the DYNACAL® PERMEATION DEVICE listed below is certified traceable to N.I.S.T. standards.

Serial Number: 89-37137

Certification Date: May 12, 2011	Certificate Expires: May 11, 2012
Chemical: Dimethyl Disulfide	Part Number: 103-040-6301-C30
Device Type: Dynacal Tube	Length: 4.00
Permeation Rate: 30.86 ng/min	Temperature: 30 C
True Accuracy: +/- 1.08 ng/min	Max Allowed Accuracy: +/- 2.00 ng/min
Certification Method: Gravimetric	Order No: 105731
Customer: BRUKER DALTONICS INC.	

Approved By: __________

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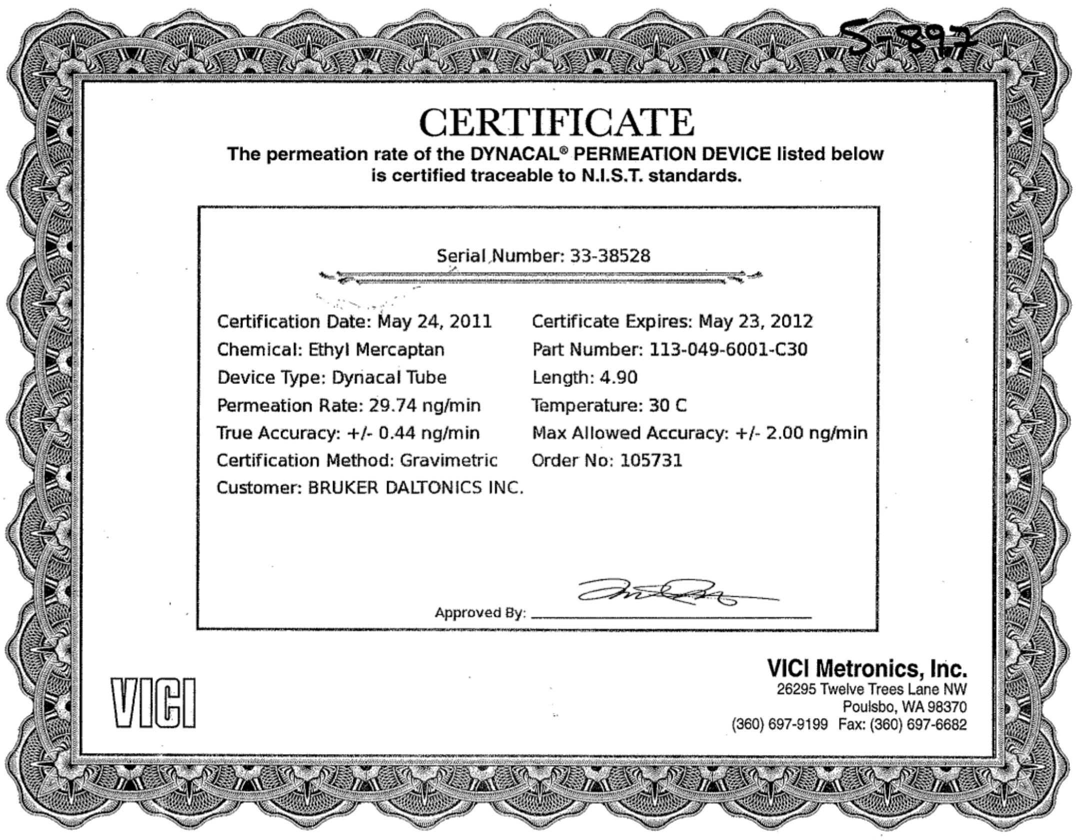
26295 Twelve Trees Lane NW
Poulsbo, WA 98370
(360) 697-9199 Fax: (360) 697-6682



S-897

CERTIFICATE

The permeation rate of the DYNACAL® PERMEATION DEVICE listed below is certified traceable to N.I.S.T. standards.

Serial Number: 33-38528

Certification Date: May 24, 2011	Certificate Expires: May 23, 2012
Chemical: Ethyl Mercaptan	Part Number: 113-049-6001-C30
Device Type: Dynacal Tube	Length: 4.90
Permeation Rate: 29.74 ng/min	Temperature: 30 C
True Accuracy: +/- 0.44 ng/min	Max Allowed Accuracy: +/- 2.00 ng/min
Certification Method: Gravimetric	Order No: 105731
Customer: BRUKER DALTONICS INC.	

Approved By: __________

VICI

VICI Metronics, Inc.
26295 Twelve Trees Lane NW
Poulsbo, WA 98370
(360) 697-9199 Fax: (360) 697-6682

Source: DMS Hydrogen Laboratory

Appendix F: California Laws and Regulations Pertaining to Hydrogen Fuel

A link to the latest version of the complete Weights and Measures code sections and related regulations can be found on the DMS homepage under "California Business and Professions Code Division 5 Weights and Measures Pertaining to Hydrogen Fuel, Chapter 2 Administration" (http://www.cdfa.ca.gov/dms/publications.html).

The most recent text of NIST *Handbook 44* Section 3.39 as found in Barclays Official California Code of Regulations can be found on the NIST publications webpage under "Section 3" (https://www.nist.gov/pml/weights-and-measures/publications/nist-handbooks/other-nist-handbooks/other-nist-handbooks-2-3).

Section 2.32 from the NIST *Handbook 130* Regulations for the Retail Sale of Hydrogen Fuel is included below.

2.32 Retail Sales of Hydrogen Fuel (H).

2.32.1 Definitions for Hydrogen Fuel. – A fuel composed of molecular hydrogen intended for consumption in a surface vehicle or electricity production device with an internal combustion engine or fuel cell. (Amended 2012)

2.32.2 Method of Retail Sale and Dispenser Labeling. – All hydrogen fuel kept, offered, or exposed for sale and sold at retail shall be in mass units in terms of the kilogram. The symbol for hydrogen vehicle fuel shall be the capital letter "H" (the word Hydrogen may also be used).

2.32.3 Retail Dispenser Labeling.

(a) A computing dispenser must display the unit price in whole cents on the basis of price per kilogram.

(b) The service pressure(s) of the dispenser must be conspicuously shown on the user interface in bar or the SI unit of pascal (Pa) (e.g., MPa).

(c) The product identity must be shown in a conspicuous location on the dispenser.

(d) National Fire Protection Association (NFPA) labeling requirements also apply.

(e) Hydrogen shall be labeled in accordance with 16 CFR 309 – FTC Labeling Alternative Fuels.

2.32.4 Street Sign Prices and Advertisements.

(a) The unit price must be in terms of price per kilogram in whole cents (e.g., $3.49 per kg, not $3.499 per kg.)

(b) The sign or advertisement must include the service pressure (expressed in megapascals) at which the dispenser(s) delivers hydrogen fuel (e.g., H35 or H70). (added 2010)

Appendix G: Hydrogen Field Standard Parts and Identification List

Customer: California Department of Food and Agriculture Division of Measurement Standards

Contact: Norman Ingram, Norm.Ingram@cdfa.ca.gov

Supplier: National Renewable Energy Laboratory

Contact: Rob Burgess, Robert.Burgess@nrel.gov

Table G-1: Instrumentation

Description	Manufacturer	Part Number	Accuracy	Comments
Measuring Scales	Sartorius	IS150IGG-H	± 1 gram	Temperature compensated
Pressure Transducers	American Sensor Tech	AST2000X00900B 1F1494	± 0.5% BFSL	Stability (1 year) ± 0.25% FS
Thermocouples	Ultra Precise	P-M-1/10	1/10 of display indication	
Flow Meters	Rheonik	RHM04 Coriolis FM	0.50%	Between 10 and 0.2 kg/min

Source: DMS Hydrogen Laboratory

Table G-2: Hydrogen Field Standard Components

Description	Type	Manufacturer	Part Number	MAWP (psi)	Temp. Range (°C)
Inlet Connections	Nozzle Receptacle	WEH	TN1 H2 70 MPa	12,690 psi	-40 °C to 85 °C
On-Board Hydrogen Tanks	Process Tank 1 (58 liters W.V.)	Dynetek	M058H700G6N-06C	12,690 psi	-40 °C to 85 °C
	Process Tank 2 (65 liters W.V.)	Lincoln Composites	RG102B20-02727	12,690 psi	-40 °C to 85 °C
Tubing	Process Tubing	High Pressure Equipment Company	29-9M6-316	20,000 psi	-250 °C to 600 °C
	Process Hoses	Spir Star	Type 6/2 Hose	14,500 psi	-30 °C to 60 °C

Description	Type	Manufacturer	Part Number	MAWP (psi)	Temp. Range (°C)
Valves	Ball Valves	High Pressure Equipment Company	20-71LF6	20,000 psi	Up to 175 °C
	Straight Valves	High Pressure Equipment Company	20-11LF6	20,000 psi	Up to 230 °C
	Check Valves	High Pressure Equipment Company	20-41LF6	20,000 psi	-
Tubing	Process Tubing	High Pressure Equipment Company	29-9M6-316	20,000 psi	-250 °C to 600 °C
	Process Hoses	Spir Star	Type 6/2 Hose	14,500 psi	-30 °C to 60 °C
Valves	Ball Valves	High Pressure Equipment Company	20-71LF6	20,000 psi	Up to 175 °C
	Straight Valves	High Pressure Equipment Company	20-11LF6	20,000 psi	Up to 230 °C
	Check Valves	High Pressure Equipment Company	20-41LF6	20,000 psi	-
	Pressure Relief Valves	High Pressure Equipment Company	HIP-20RV	20,000 psi	Up to 150 °C
	Temperature Relief Valves	Dynetek	PRD-700-01-0	12,691 psi	-40 °C to 85 °C Set at 110 °C
Fittings	Process Tees	High Pressure Equipment Company	20-23LF6	20,000 psi	-
	Process Elbows	High Pressure Equipment Company	20-22LF6	20,000 psi	-
	Hose Couplings	Spir Star	SPC-600	20,000 psi	-

Source: DMS Hydrogen Laboratory

Appendix H: Certificates of Analysis of Biodiesel and No. 2 Diesel Blend Stocks

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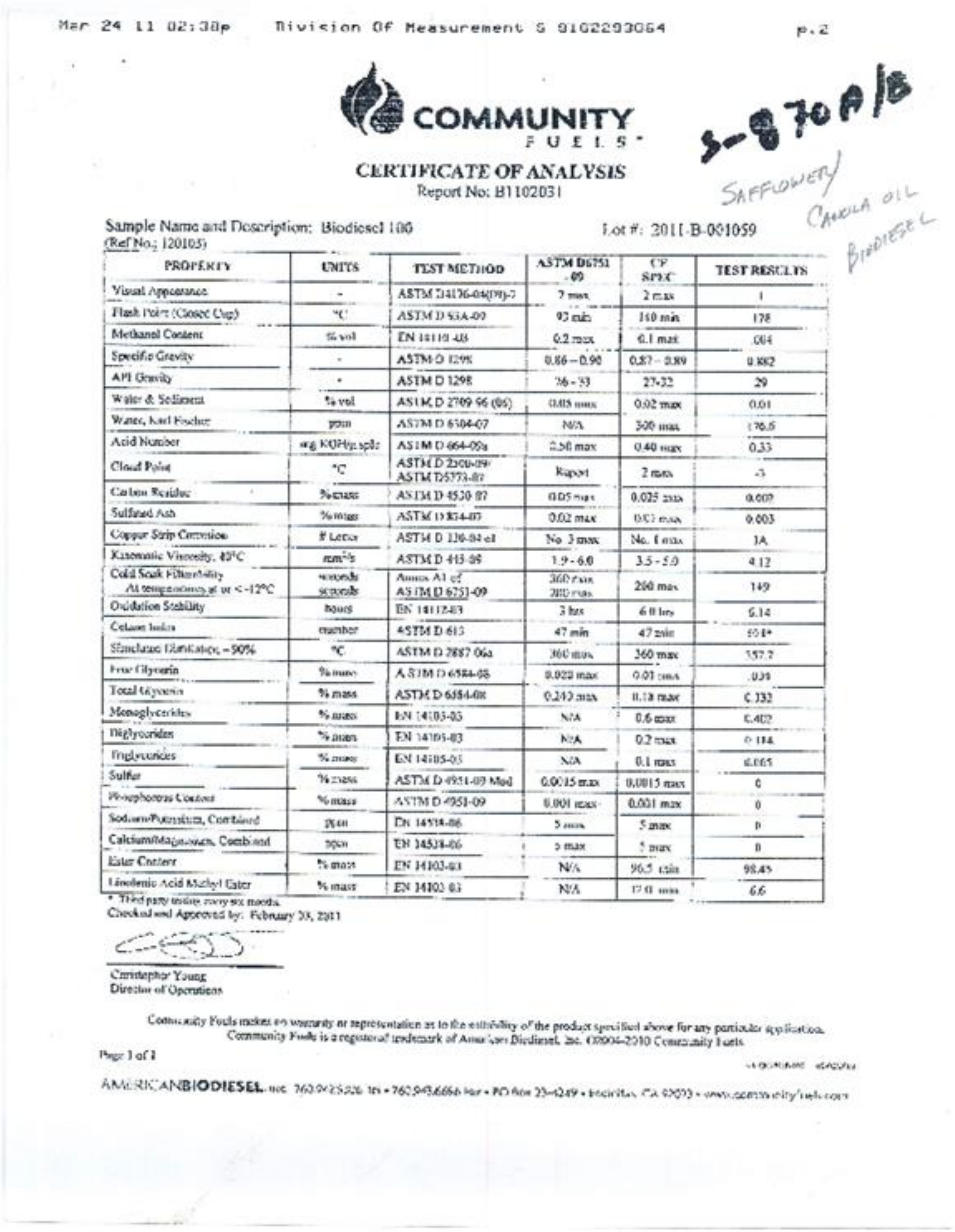
Figure H-1: Certificate of Analysis for Community Fuels Safflower/Canola B100



Mar 24 11 02:38p Division Of Measurement S 9162293064 p.2

COMMUNITY FUELS

S-870A/B

SAFFLOWER/ CANOLA OIL BIODIESEL

CERTIFICATE OF ANALYSIS

Report No: B1102031

Sample Name and Description: Biodiesel 100 Lot #: 2011-B-001059
(Ref No.: 120105)

PROPERTY	UNITS	TEST METHOD	ASTM D6751 -09	CF SPEC	TEST RESULTS
Visual Appearance	-	ASTM D4176-04(09)-2	2 max	2 max	1
Flash Point (Closed Cup)	°C	ASTM D 93A-09	93 min	160 min	178
Methanol Content	% vol	EN 14110-03	0.2 max	0.1 max	.004
Specific Gravity	-	ASTM D 1298	0.86 – 0.90	0.87 – 0.89	0.882
API Gravity	-	ASTM D 1298	26 - 33	27-32	29
Water & Sediment	% vol	ASTM D 2709 96 (06)	0.05 max	0.02 max	0.01
Water, Karl Fischer	ppm	ASTM D 6304-07	N/A	300 max	176.6
Acid Number	mg KOH/g sple	ASTM D 664-09a	0.50 max	0.40 max	0.33
Cloud Point	°C	ASTM D 2500-09/ ASTM D5773-07	Report	2 max	-3
Carbon Residue	% mass	ASTM D 4530 07	0.05 max	0.025 max	0.007
Sulfated Ash	% mass	ASTM D 874-07	0.02 max	0.01 max	0.003
Copper Strip Corrosion	# Letter	ASTM D 130-04 e1	No. 3 max	No. 1 max	1A
Kinematic Viscosity, 40°C	mm²/s	ASTM D 445-06	1.9 - 6.0	3.5 - 5.0	4.12
Cold Soak Filterability At temperatures at or < -12°C	seconds seconds	Annex A1 of ASTM D 6751-09	360 max 200 max	200 max	149
Oxidation Stability	hours	EN 14112-03	3 hrs	6.0 hrs	6.14
Cetane Index	number	ASTM D 613	47 min	47 min	55.1*
Simulated Distillation, - 90%	°C	ASTM D 2887 06a	360 max	360 max	357.2
Free Glycerin	% mass	ASTM D 6584-08	0.020 max	0.01 max	.009
Total Glycerin	% mass	ASTM D 6584-08	0.240 max	0.18 max	0.132
Monoglycerides	% mass	EN 14105-03	N/A	0.6 max	0.402
Diglycerides	% mass	EN 14105-03	N/A	0.2 max	0.114
Triglycerides	% mass	EN 14105-03	N/A	0.1 max	0.065
Sulfur	% mass	ASTM D 4951-09 Mod	0.0015 max	0.0015 max	0
Phosphorous Content	% mass	ASTM D 4951-09	0.001 max	0.001 max	0
Sodium/Potassium, Combined	ppm	EN 14538-06	5 max	5 max	0
Calcium/Magnesium, Combined	ppm	EN 14538-06	5 max	5 max	0
Ester Content	% mass	EN 14103-03	N/A	96.5 min	98.45
Linolenic Acid Methyl Ester	% mass	EN 14103 03	N/A	12.0 max	6.6

* Third party testing every six months.

Checked and Approved by: February 28, 2011

Christopher Young
Director of Operations

Community Fuels makes no warranty or representation as to the suitability of the product specified above for any particular application. Community Fuels is a registered trademark of American Biodiesel, Inc. ©2004-2010 Community Fuels.

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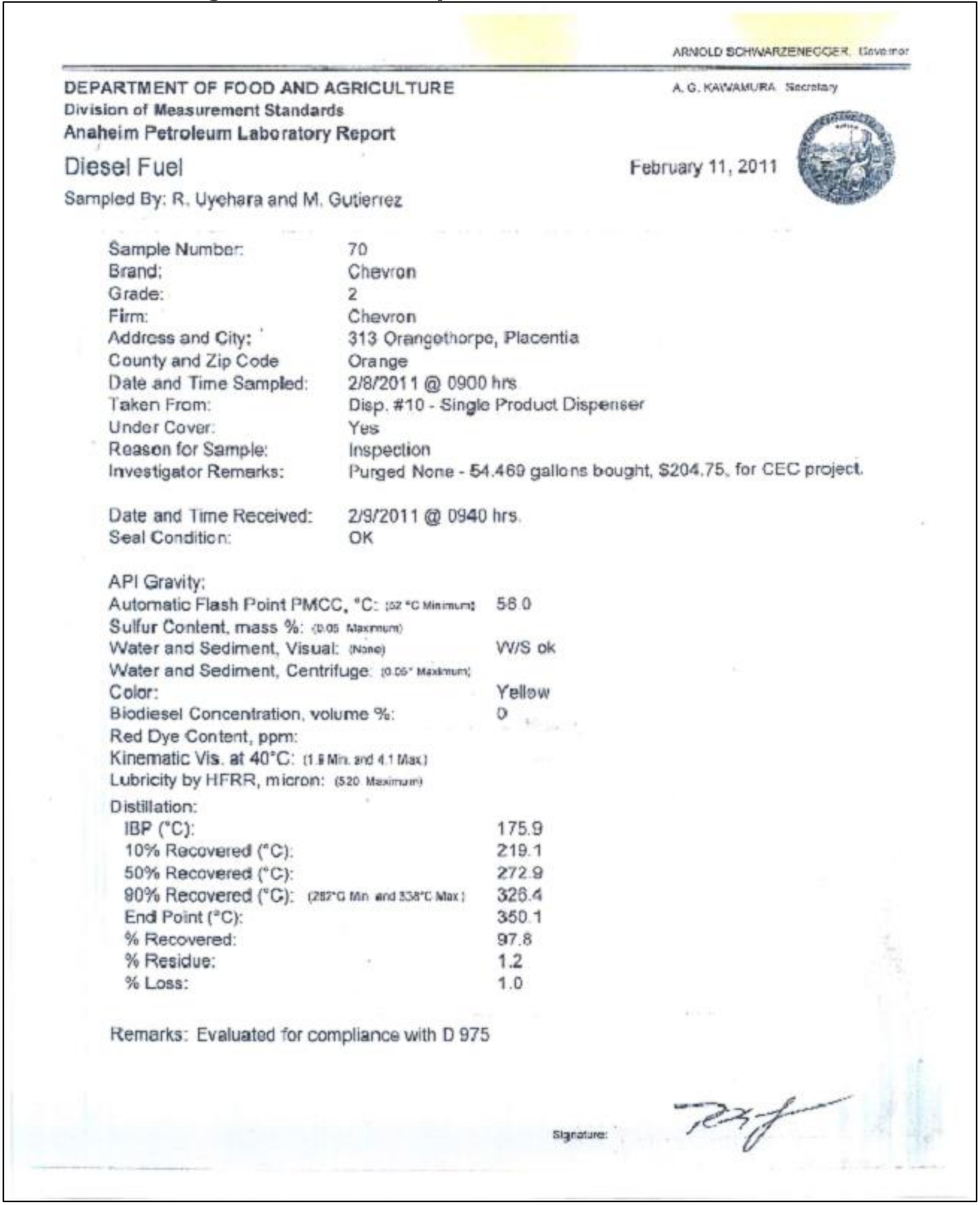
Source: DMS Hydrogen Laboratory

Figure H-2: DMS Analysis of Petroleum Diesel Stock



ARNOLD SCHWARZENEGGER, Governor

A. G. KAWAMURA, Secretary

DEPARTMENT OF FOOD AND AGRICULTURE
Division of Measurement Standards
Anaheim Petroleum Laboratory Report

Diesel Fuel

February 11, 2011

Sampled By: R. Uyehara and M. Gutierrez

Sample Number:	70
Brand:	Chevron
Grade:	2
Firm:	Chevron
Address and City:	313 Orangethorpe, Placentia
County and Zip Code	Orange
Date and Time Sampled:	2/8/2011 @ 0900 hrs
Taken From:	Disp. #10 - Single Product Dispenser
Under Cover:	Yes
Reason for Sample:	Inspection
Investigator Remarks:	Purged None - 54.469 gallons bought, $204.75, for CEC project.
Date and Time Received:	2/9/2011 @ 0940 hrs.
Seal Condition:	OK

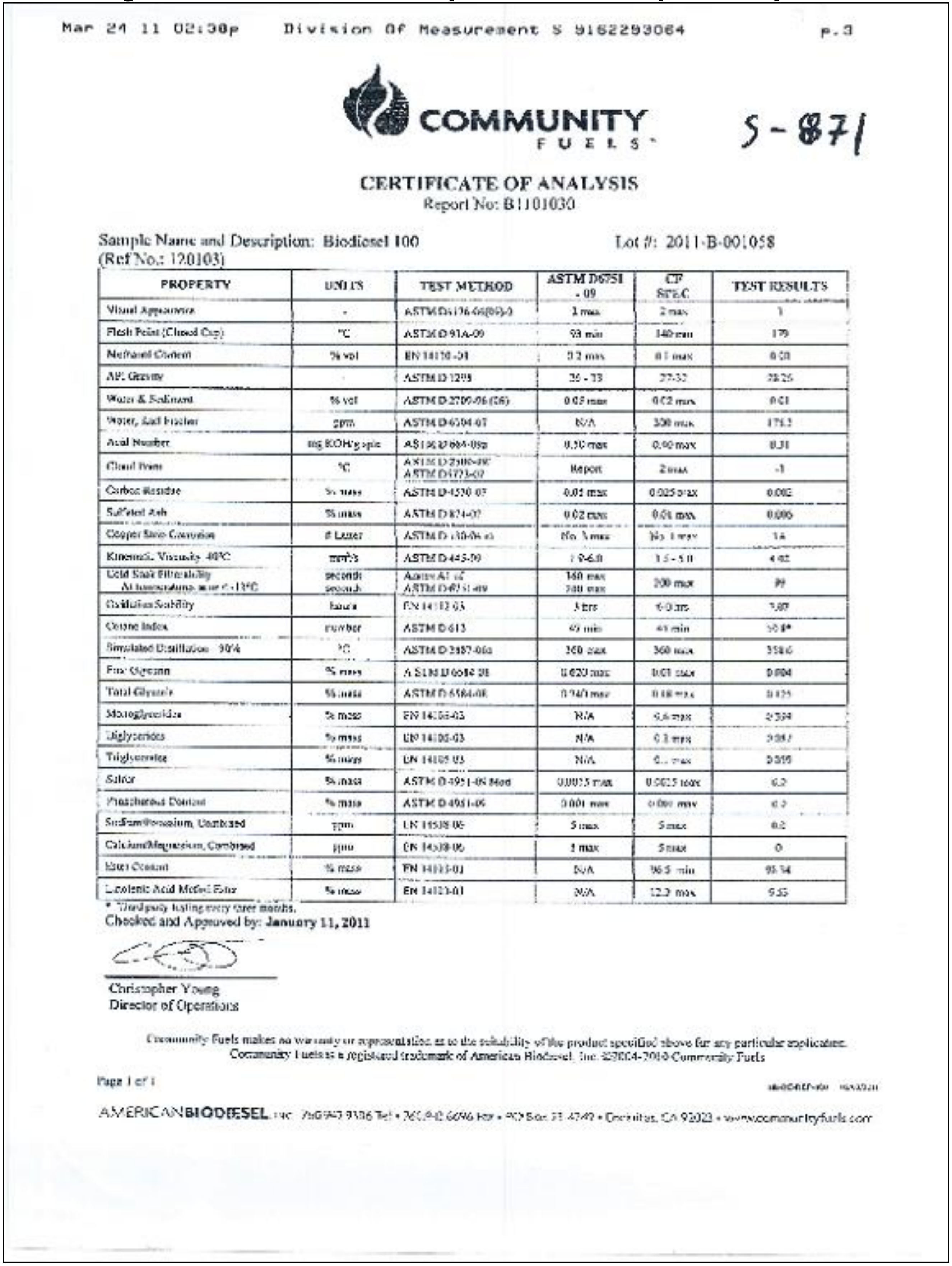
API Gravity:	
Automatic Flash Point PMCC, °C: (52 °C Minimum)	56.0
Sulfur Content, mass %: (0.05 Maximum)	
Water and Sediment, Visual: (None)	W/S ok
Water and Sediment, Centrifuge: (0.05% Maximum)	
Color:	Yellow
Biodiesel Concentration, volume %:	0
Red Dye Content, ppm:	
Kinematic Vis. at 40°C: (1.9 Min. and 4.1 Max.)	
Lubricity by HFRR, micron: (520 Maximum)	
Distillation:	
IBP (°C):	175.9
10% Recovered (°C):	219.1
50% Recovered (°C):	272.9
90% Recovered (°C): (282°C Min and 338°C Max)	326.4
End Point (°C):	350.1
% Recovered:	97.8
% Residue:	1.2
% Loss:	1.0

Remarks: Evaluated for compliance with D 975

Signature:

Source: DMS Hydrogen Laboratory

Figure H-3: Certificate of Analysis for Community Fuels Soy B100



Mar 24 11 02:30p Division Of Measurement S 9162293064 p.3

COMMUNITY FUELS

S-871

CERTIFICATE OF ANALYSIS

Report No: B1101030

Sample Name and Description: Biodiesel 100 Lot #: 2011-B-001058
(Ref No.: 120103)

PROPERTY	UNITS	TEST METHOD	ASTM D6751 - 09	CF SPEC	TEST RESULTS
Visual Appearance	-	ASTM D4176-04(09)-1	1 max	2 max	1
Flash Point (Closed Cup)	°C	ASTM D 93A-09	93 min	140 min	179
Methanol Content	% vol	EN 14110-03	0.2 max	0.1 max	0.00
API Gravity	-	ASTM D 1298	26 - 33	27-32	28.25
Water & Sediment	% vol	ASTM D 2709-96 (06)	0.05 max	0.02 max	0.01
Water, Karl Fischer	ppm	ASTM D 6304-07	N/A	300 max	175.3
Acid Number	mg KOH/g sple	ASTM D 664-09a	0.50 max	0.40 max	0.31
Cloud Point	°C	ASTM D 2500-09 ASTM D5773-07	Report	2 max	-1
Carbon Residue	% mass	ASTM D 4530-07	0.05 max	0.025 max	0.002
Sulfated Ash	% mass	ASTM D 874-07	0.02 max	0.01 max	0.006
Copper Strip Corrosion	# Letter	ASTM D 130-04 e1	No. 3 max	No. 1 max	1A
Kinematic Viscosity 40°C	mm²/s	ASTM D 445-09	1.9-6.0	3.5 - 5.0	4.02
Cold Soak Filterability At temperatures at or < -12°C	seconds seconds	Annex A1 of ASTM D 6751-09	360 max 200 max	200 max	99
Oxidation Stability	hours	EN 14112-03	3 hrs	6.0 hrs	7.07
Cetane Index	number	ASTM D 613	47 min	45 min	50.8*
Simulated Distillation - 90%	°C	ASTM D 2887-06a	360 max	360 max	358.6
Free Glycerin	% mass	ASTM D 6584-08	0.020 max	0.01 max	0.004
Total Glycerin	% mass	ASTM D 6584-08	0.240 max	0.18 max	0.125
Monoglycerides	% mass	EN 14105-03	N/A	0.6 max	0.394
Diglycerides	% mass	EN 14105-03	N/A	0.2 max	0.087
Triglycerides	% mass	EN 14105-03	N/A	0.2 max	0.055
Sulfur	% mass	ASTM D 4951-06 Mod	0.0015 max	0.0015 max	0.2
Phosphorous Content	% mass	ASTM D 4951-06	0.001 max	0.001 max	0.2
Sodium/Potassium, Combined	ppm	EN 14538-06	5 max	5 max	0.2
Calcium/Magnesium, Combined	ppm	EN 14538-06	5 max	5 max	0
Ester Content	% mass	EN 14103-01	N/A	96.5 min	95.34
Linolenic Acid Methyl Ester	% mass	EN 14103-01	N/A	12.0 max	5.55

* Third party testing every three months.

Checked and Approved by: January 11, 2011

Christopher Young
Director of Operations

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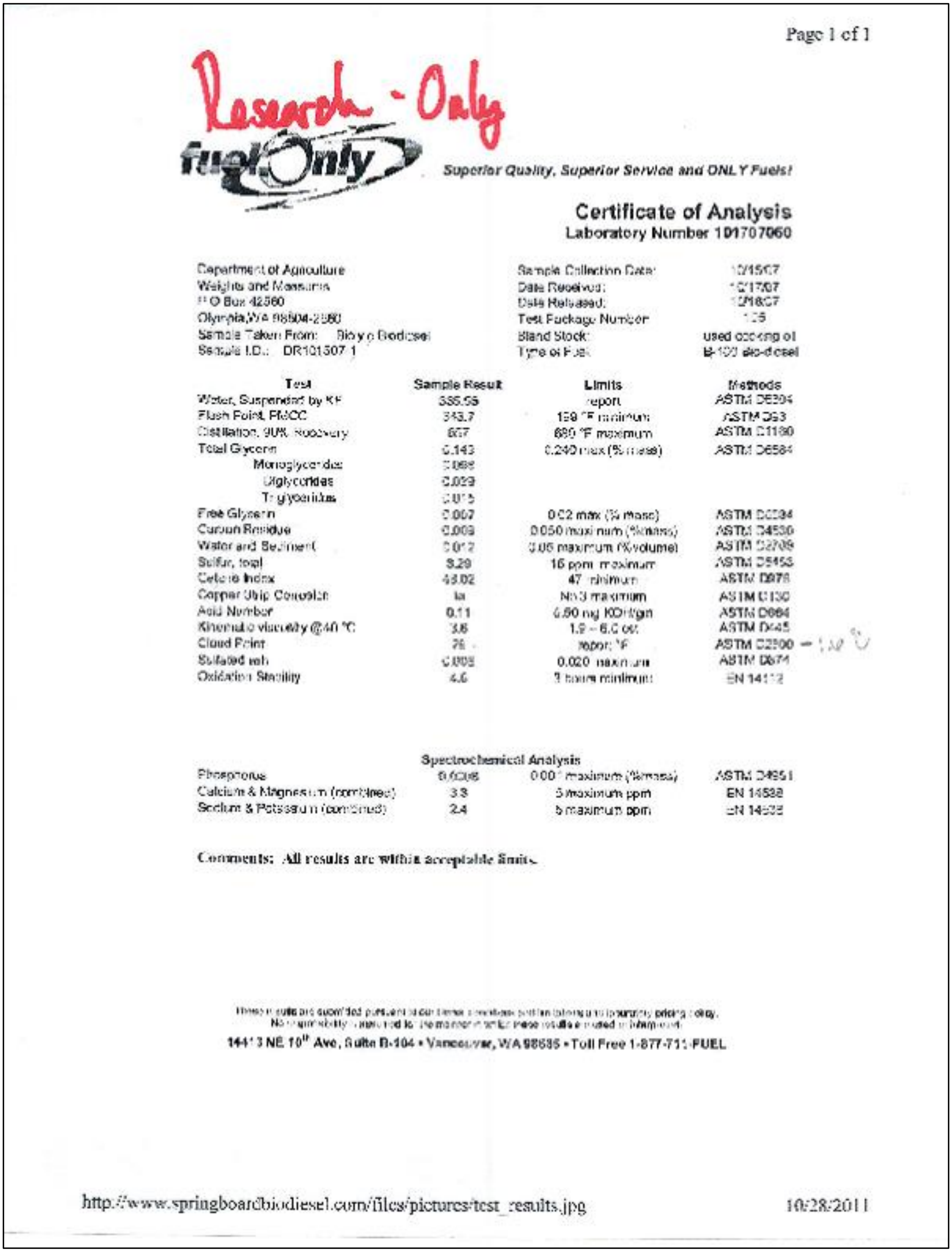
Source: DMS Hydrogen Laboratory

Figure H-4: Certificate of Analysis for Yellow Grease B100



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Research - Only

fuelOnly

Superior Quality, Superior Service and ONLY Fuels!

Certificate of Analysis

Laboratory Number 101707060

Department of Agriculture
Weights and Measures
P O Box 42560
Olympia,WA 98504-2560
Sample Taken From: [illegible] Biodiesel
Sample I.D.: DR101507 1

Sample Collection Date: 10/15/07
Date Received: 10/17/07
Date Released: 10/18/07
Test Package Number: 105
Blend Stock: used cooking oil
Type of Fuel: B-100 bio-diesel

Test	Sample Result	Limits	Methods
Water, Suspended by KF	335.56	report	ASTM D6304
Flash Point, PMCC	343.7	130 °F minimum	ASTM D93
Distillation, 90% Recovery	667	680 °F maximum	ASTM D1160
Total Glycerin	0.143	0.240 max (% mass)	ASTM D6584
Monoglycerides	0.098		
Diglycerides	0.029		
Triglycerides	0.015		
Free Glycerin	0.007	0.02 max (% mass)	ASTM D6584
Carbon Residue	0.009	0.050 maximum (%mass)	ASTM D4530
Water and Sediment	0.012	0.05 maximum (%volume)	ASTM D2709
Sulfur, total	3.29	15 ppm maximum	ASTM D5453
Cetane Index	48.02	47 minimum	ASTM D976
Copper Strip Corrosion	1a	No 3 maximum	ASTM D130
Acid Number	0.11	0.50 mg KOH/gm	ASTM D664
Kinematic viscosity @40 °C	3.8	1.9 – 6.0 cst	ASTM D445
Cloud Point	76	report °F	ASTM D2500 – 1.2 °C
Sulfated ash	0.005	0.020 maximum	ASTM D874
Oxidation Stability	4.6	3 hours minimum	EN 14112

Spectrochemical Analysis

Phosphorus	0.0006	0.001 maximum (%mass)	ASTM D4951
Calcium & Magnesium (combined)	3.3	5 maximum ppm	EN 14538
Sodium & Potassium (combined)	2.4	5 maximum ppm	EN 14538

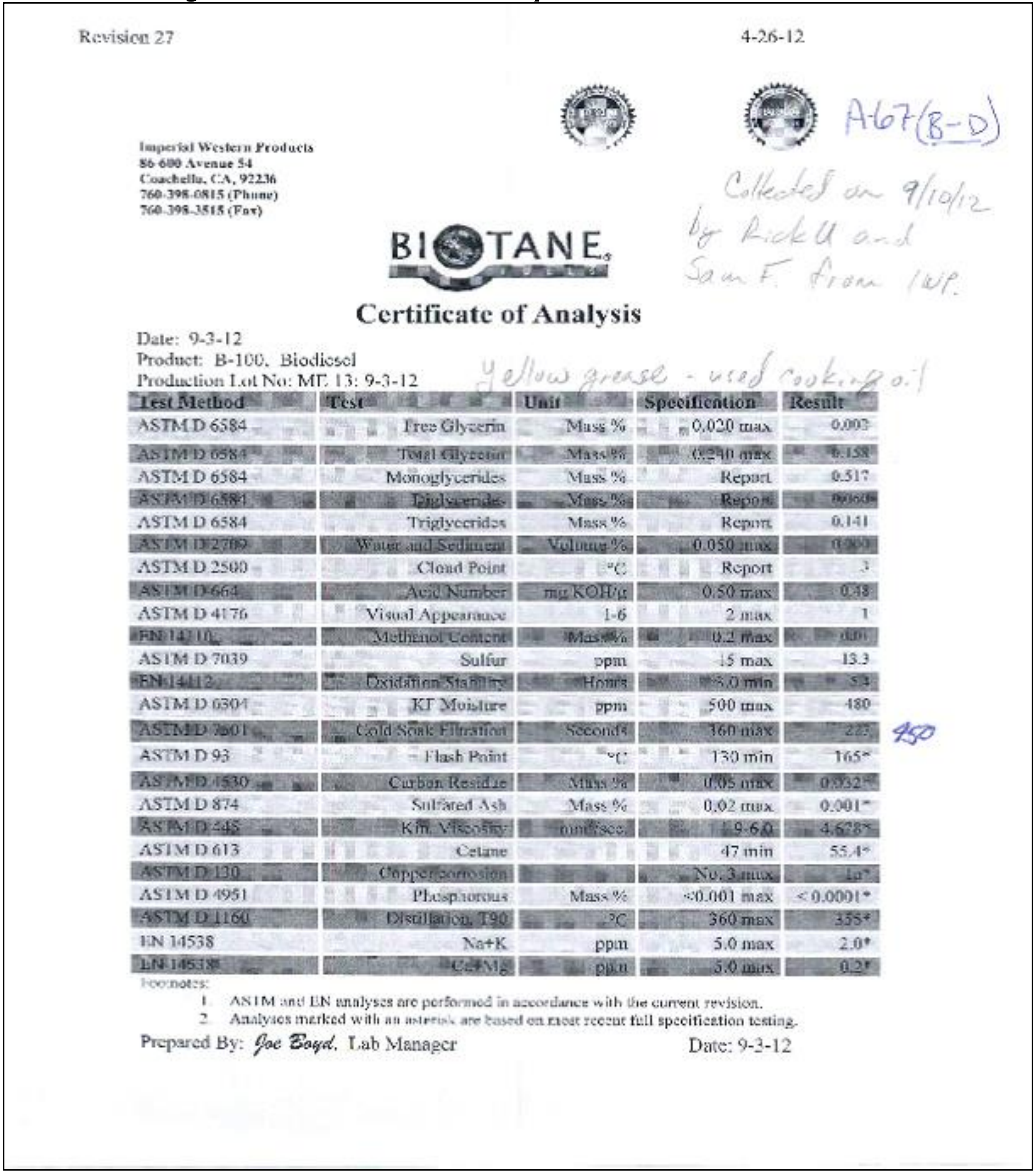
Comments: All results are within acceptable limits.

14413 NE 10th Ave, Suite B-104 • Vancouver, WA 98685 • Toll Free 1-877-711-FUEL

http://www.springboardbiodiesel.com/files/pictures/test_results.jpg 10/28/2011

Source: DMS Hydrogen Laboratory

Figure H-5: Certificate of Analysis for Yellow Grease B100



Revision 27 4-26-12

A-67 (B-D)

Imperial Western Products
86-600 Avenue 54
Coachella, CA, 92236
760-398-0815 (Phone)
760-398-3515 (Fax)

Collected on 9/10/12
by Rick U and
Sam F. from IWP.

BIOTANE

Certificate of Analysis

Date: 9-3-12
Product: B-100, Biodiesel
Production Lot No: MF 13: 9-3-12

yellow grease - used cooking oil

Test Method	Test	Unit	Specification	Result
ASTM D 6584	Free Glycerin	Mass %	0.020 max	0.002
ASTM D 6584	Total Glycerin	Mass %	0.240 max	0.158
ASTM D 6584	Monoglycerides	Mass %	Report	0.517
ASTM D 6584	Diglycerides	Mass %	Report	[illegible]
ASTM D 6584	Triglycerides	Mass %	Report	0.141
ASTM D 2709	Water and Sediment	Volume %	0.050 max	0.000
ASTM D 2500	Cloud Point	°C	Report	3
ASTM D 664	Acid Number	mg KOH/g	0.50 max	0.48
ASTM D 4176	Visual Appearance	1-6	2 max	1
EN 14110	Methanol Content	Mass %	0.2 max	0.01
ASTM D 7039	Sulfur	ppm	15 max	13.3
EN 14112	Oxidation Stability	Hours	3.0 min	5.3
ASTM D 6304	KF Moisture	ppm	500 max	480
ASTM D 7501	Cold Soak Filtration	Seconds	360 max	223
ASTM D 93	Flash Point	°C	130 min	165*
ASTM D 4530	Carbon Residue	Mass %	0.05 max	0.032*
ASTM D 874	Sulfated Ash	Mass %	0.02 max	0.001*
ASTM D 445	Kin. Viscosity	mm²/sec.	1.9-6.0	4.678*
ASTM D 613	Cetane		47 min	55.4*
ASTM D 130	Copper corrosion		No. 3 max	1a*
ASTM D 4951	Phosphorous	Mass %	<0.001 max	< 0.0001*
ASTM D 1160	Distillation, T90	°C	360 max	355*
EN 14538	Na+K	ppm	5.0 max	2.0*
EN 14538	Ca+Mg	ppm	5.0 max	0.2*

450

Footnotes:

1. ASTM and EN analyses are performed in accordance with the current revision.
2. Analyses marked with an asterisk are based on most recent full specification testing.

Prepared By: *Joe Boyd*, Lab Manager Date: 9-3-12

Source: DMS Hydrogen Laboratory