biofuels analysis

support and solutions for your lab

PerkinElmer®
precisely.

Who is PerkinElmer?

With proven leadership in product innovation, including the introduction of the first commercial instruments in Infrared Spectroscopy (IR), Gas Chromatography (GC), and Graphite Furnace Atomic Absorption (GFAA) Spectroscopy, PerkinElmer continues to make advances in systems, providing improved analytical capabilities and ease-of-use. Other innovations, from the use of capillary columns for GC and a solid-state detector designed specifically for Inductively Coupled Plasma (ICP-OES), to our latest systems that operate via touch-screen control in multiple languages, demonstrate our continued commitment to providing state-of-the-art analytical capabilities. PerkinElmer has the business acumen of a global company plus the knowledge to facilitate your business processes.

What do you need in today's biofuels laboratory?

- Analytical capability to perform the required methods
- Delivery of the system you need and after-sale support, such as training, to help you get started rapidly
- Cost-effective packages covering the full range of laboratory needs

Whether you are an established laboratory or a new startup in this industry, your laboratory needs will be met and your business will run smoothly.

Analyses for quality

Within the last few years, there has been increasing interest in replacing petroleum oil and natural-gas-based products with biomass-based products. One of the most important benefits of this approach is a more predictable feedstock, free from the variable price and decreasing supply of petroleum-based feedstocks. Another benefit is less pollution, increasingly important as the population grows. Although biomass products have not been cost-competitive in the past, the increasing cost of oil and decreasing cost of biomass products due to advanced technology have brought the prices of these two approaches into balance.

Biomass products do not mean only fuels (biofuels), but also other products that are traditionally derived from petroleum oil (or gas), such as plastics, rubber, lubricants and chemicals. Biofuels, such as ethanol and biodiesel, have had the most recent publicity, driven by recent regulations to reduce dependence on mineral oil (USDA Federal Biobased Products Preferred Procurement Program (FB4P), EU Directive (2003/30/EC)). Consumer acceptance of the drive to substitute or blend some of the current mineral-based fuel with biomass fuel in gasoline and diesel is receiving widespread recognition and support.

Measurements are important in all of these processes, from feedstock to final biobased end-product. Reliable production and minimization of pollution depend upon knowledge of the feedstock components and evaluation of the final product quality.

Shown in Table 1 are some of the tests required for biodiesel-quality evaluation as specified by the American Society for Testing and Materials (ASTM). Similar ASTM criteria are shown for ethanol in Table 2.

Table 1. ASTM Standard D6751 Criteria for Biodiesel.

Property	ASTM test method	Limits	Units
Flash point (closed cup)	D93	130.0 min	˚C
Water and sediment	D2709	0.050 max	% volume
Kinematic viscosity, 40 ˚C	D445	1.9-6.0	mm^2/s
Sulfated ash	D874	0.020 max	% mass
Sulfur Grade S15	D5453	0.0015 max (15)	% mass (ppm)
Grade S500		0.05 (500) max	
Copper strip corrosion	D130	No. 3 max	
Cetane number	D613	47 min	
Cloud point	D2500	Report	˚C
Carbon residue	D4530	0.050 max	% mass
Acid number	D664	0.50 max	mg KOH/g
Free glycerin	D6584	0.020	% mass
Total glycerin	D6584	0.240	% mass
Phosphorus content	D4951	0.001 max	% mass
Distillation temperature, Atmospheric equivalent temperature, 90% recovered	D1160	360	˚C

Table 2. ASTM Standard D4806 for Ethanol used for Fuel.

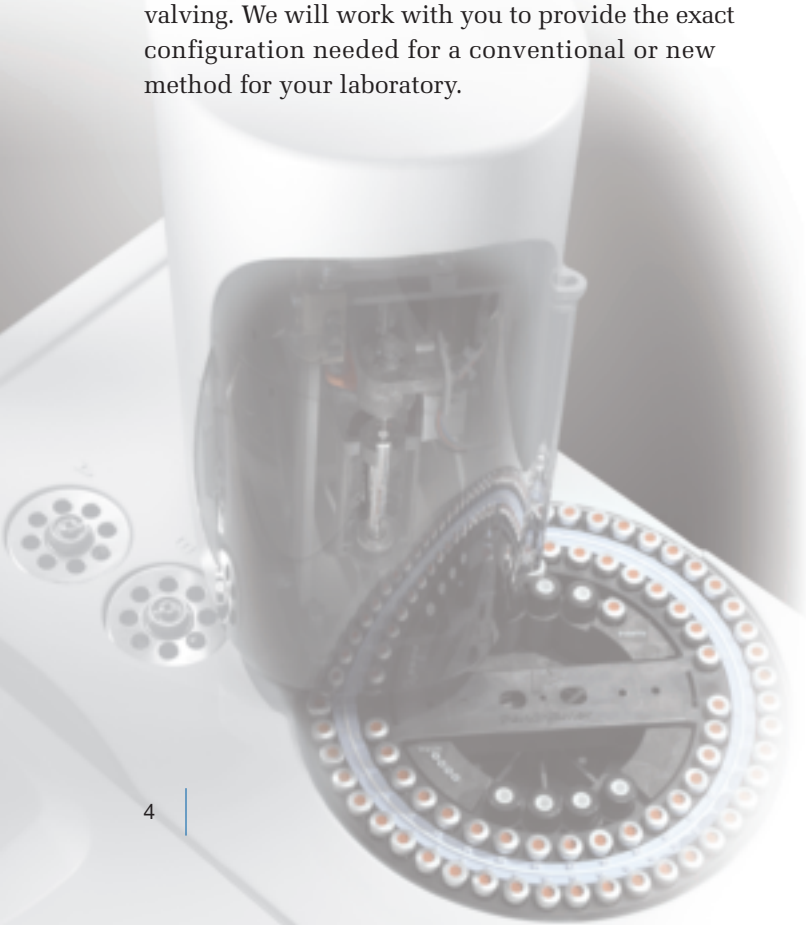
Property	Limits	Units
Ethanol	92.1 min	%v/v
Methanol	0.5 max (5,000 ppm)	%v/v
Water	1.0 max (10,000 ppm)	%v/v
Solvent-washed gum	5 max (50 ppm)	mg/100 mL
Chloride ion	40 max (40 ppm)	mg/L
Copper content	0.1 max (0.1 ppm)	mg/kg
Acidity, as acetic acid	0.007 max (70 ppm)	%w/w
Appearance	Visibly free of suspended or precipitated contaminants (clear and bright).	
Denaturant	A minimum of 1.96% v/v, and a maximum of 4.76% v/v of natural gasoline, gasoline components or unleaded gasoline.	

organics analysis from sample handling to detection

Gas chromatography for complete evaluation

Biodiesel can provide a product for blending with petroleum-based diesel fuel that provides reduced sulfur content, reduced emissions and increased lubricity. Analysis of the finished biodiesel for contaminants or by-products is critical in ensuring the best engine performance without clogging the fuel system or causing injector fouling.

Gas chromatography (GC) is a key analytical technique for biofuels analysis. PerkinElmer offers a complete family of gas chromatography products that can carry out these determinations and are optimized for performance and reliability. The Clarus® family of GCs supports a variety of detectors, such as flame ionization, thermal conductivity, mass spectrometry and others. TurboMatrix™ Headspace and Thermal Desorption sample-handling accessories streamline the sampling and introduction of volatile components into the GC. PerkinElmer partners with Arnel, Inc. to provide turnkey GC systems for analyses requiring specific valving. We will work with you to provide the exact configuration needed for a conventional or new method for your laboratory.



Testing the quality of biodiesel is a challenge for both manufacturers and blenders of biodiesel fuel. The challenges for laboratories analyzing biodiesel are many. Several mechanisms for the conversion of the free fatty acids (lipids) to fatty acid esters have been published. These mechanisms include hydrolysis, saponification, transesterification and esterification. Esterification is carried out by the reaction of the carboxylic acids (free fatty acids), alcohol and a catalyst. The fatty acid methyl ester (FAME) is the reaction typically used for manufacturing biodiesel fuel, with water and glycerin as by-products. The direct analysis of FAME content, as well as the glycerin by-product may be assessed for quality. Simulated distillation for boiling-point distribution is another test indication, an important characteristic of the fuel.

Although many parameters must be assessed to determine product quality, an important by-product of biodiesel production is glycerin and end-product concentration yields a rapid assessment of the quality. An example of a typical GC chromatogram is shown in Figure 2.

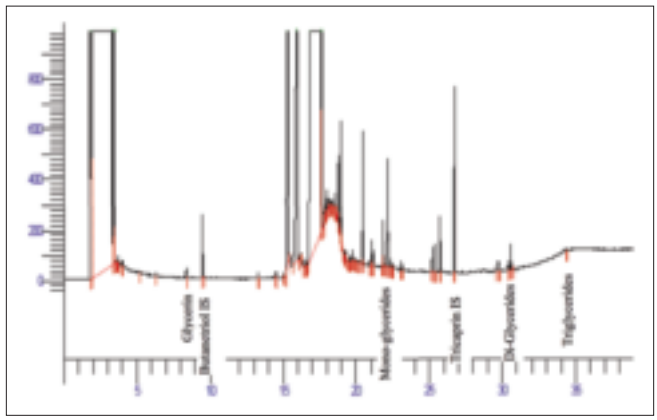


Figure 2. Free and total glycerin determination rapidly measured. Total monoglycerides are calculated with a summed peak group, including all four monoglyceride peaks, excluding the C24 carboxylic acid methyl ester peak eluting between the monoglycerides.

assuring the bio-content of fuel

Liquid scintillation analysis provides content confirmation

Liquid scintillation counting (LSC) of radiocarbon (^{14}C) can be used to determine biological content of any organic material. All living biological material has a constant amount of radiocarbon per weight unit of total carbon formed by cosmic radiation bombarding nitrogen molecules in the upper atmosphere. Radiocarbon will disappear from biological material through the radioactive decay process (half-life 5730 years). Products fully made out of fossil carbohydrates do not include radiocarbon any more since it has decayed out completely within the millions of years the product has been "underground". By determining the radiocarbon activity versus total carbon content we can tell the biological content of any organic product.

The analysis of both diesel blended with biodiesel and gasoline blended with ethanol may be required to verify the bio-based content for regulatory or tax-benefit purposes.

PerkinElmer® LSC products can perform ASTM Standard D-6866-05 – *Standard Test Methods for Determining the Biobased Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis.* Method parts A and C can be performed with LSC, offering a selection of sensitivities and sample-preparation options to meet your needs. Alternatively, a simpler method of analysis can be used, in many cases, blending the sample with a cocktail and directly analyzing the mix with LSC.

The ASTM method alternatives are compared with a direct analysis for several considerations in Table 3.

Table 3. Comparison of Methods for Bio-Content Analysis.

Method	Sample Preparation Time	Analysis Time (min)	Analysis Cost** (USD)	Instrument Cost	Sample Size	Contamination Risk***	Precision
Direct Liquid Scintillation Counting	3 minutes	330	150	Moderate	5-10 g	Low	< 3%
Method A Liquid Scintillation Counting with CO_2 trapping*	3 hours	1300	250	Moderate	0.2-1 g	Moderate	< 9%
Method B Acceleration Mass Spectrometry (AMS)*	2 hours	20	400	High	1 mg	High	< 1%
Method C Liquid Scintillation Counting with Benzene Synthesis*	3 hours	1300	250	Moderate	2-10 g	Low	< 2%

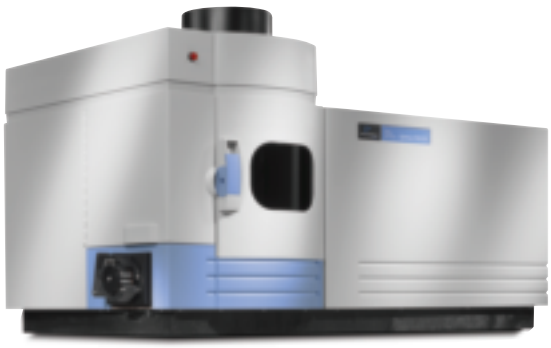
* ASTM standard method
** Includes the depreciation of equipment
*** Risk of contaminating the sample with ambient biological carbon during the process

inorganic analysis from the leader

Inorganic measurements are also part of the analysis picture. Meeting product specifications is critical to efficient and profitable plant operation. Meeting regulatory requirements, such as lower sulfur concentration in diesel fuel is also an important measurement criteria. PerkinElmer offers a wide range of inorganic measurement techniques covering the full range of metals, concentrations and matrices that might need to be evaluated. As the market leader in inorganic analysis, we are proud of our experience. We can help – from the initial instrument selection to providing delivery, support, consumables and service globally.

AAs offer the capabilities you need

Atomic Absorption (AA) spectroscopy is a moderately priced technique, suitable for routine measurements in laboratories measuring a few samples for a few elements. PerkinElmer has a complete line of AAnalyst™ AA spectrometers to fit your needs from simple, manually-operated flame systems, to sophisticated, automated graphite-furnace systems with quality-control software.



Optima 2100 ICP-OES system.

ICP-OES systems maximize productivity

For laboratories requiring measurement of more than a few elements per sample or measuring large numbers of samples, ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) is often the better choice and has become standard in many laboratories. It is also useful for elements such as sulfur and phosphorus that cannot be sensitively determined with AA. Our complete line of Optima™ ICP-OES systems can provide the productivity that fits your needs and budget. Table 4 shows several analyses of feedstock for Ca, Mg, and P to ensure a quality product. The elements can be run rapidly and precisely in less than three minutes using the Optima 2100 ICP-OES.

ICP-MS provides the ultimate in metals detection capabilities

For ultratrace measurements, ICP coupled with Mass Spectrometry (ICP-MS) is an option. Our market leading ELAN® ICP-MS systems provide flexible solutions for ultratrace metals analysis. The popular ELAN 9000 ICP-MS system provides basic ICP-MS capabilities, while the ELAN DRC-e and ELAN DRC II systems provide freedom from common interferences with groundbreaking Dynamic Reaction Cell™ (DRC™) ability to achieve the lowest detection limits in any matrix.

Table 4. Analysis of P, Ca and Mg in Biodiesel Feedstock (mg/kg) to ensure product quality.

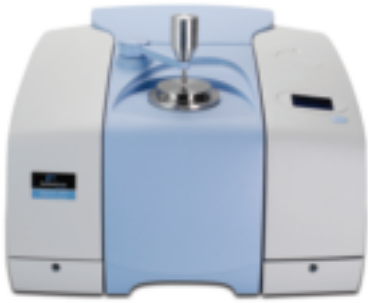
	Plant Feed			Degummed Oil			Crude Oil		
Feed Stock	P	Ca	Mg	P	Ca	Mg	P	Ca	Mg
Batch 1	7.07	0.83	0.79	30.00	3.63	3.30	448.5	57.9	54.7
Batch 2	11.63	1.48	1.45	7.89	0.72	0.72	550.7	68.3	66.1

a versatile tool for process and quality control

FT-IR provides rapid results

At different stages of the production of biofuels, it is important to monitor the process. Infrared (FT-IR) is a highly versatile technique that can be used to characterize a compound from its unique molecular vibration fingerprint. FT-IR can be used to assure the quality and identify incoming feedstocks as well as during manufacturing, monitoring the conversion process to determine the progress of reactions and the yield. Once the final product is complete, FT-IR can screen the quality of biofuel products. In research, FT-IR is employed to check the emission from biofuels, to determine the catalytic reactions in the conversion process and for other projects.

Defining the standards for FT-IR technology for over 60 years, PerkinElmer is an experienced and knowledgeable supplier of FT-IR spectrometers for laboratories worldwide. By taking a comprehensive quality approach, PerkinElmer provides the highest quality FT-IR systems that can help comply with fuel standards by rapid assessment of product quality before further analysis is performed.



Spectrum™ 100 FT-IR Spectrometer.

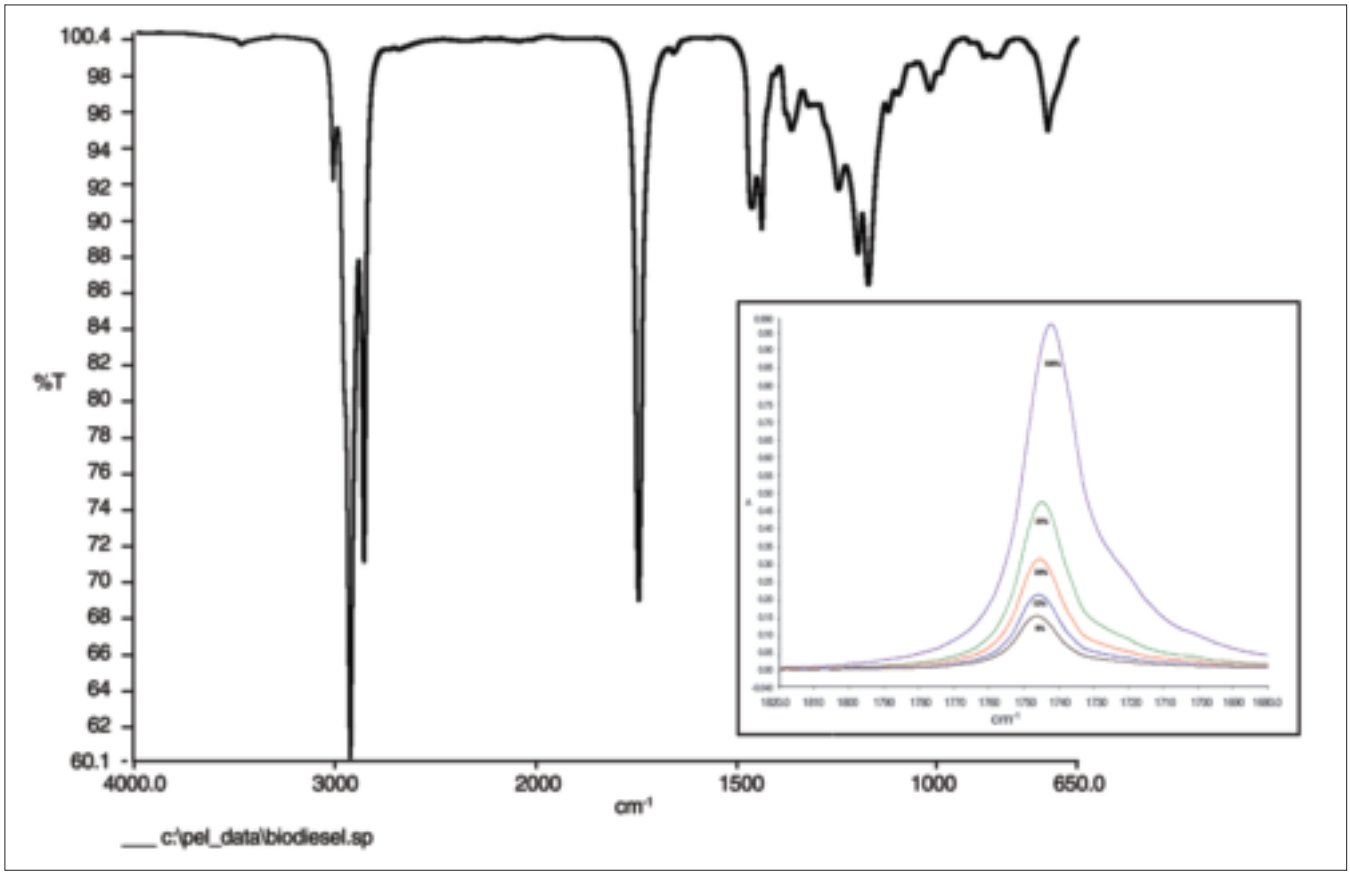


Figure 3. Biodiesel standard shown with inset of the full set of standards expanded in the spectrum region of interest for EN 14078.

PerkinElmer, Inc.

LABWORKS LIMS: robust, easy-to-use, and cost-effective

A Laboratory Information Management System (LIMS) enables efficient monitoring and reporting of critical data throughout the reaction process. Comprehensive LIMS functionality is critical for effective sample management, tracking and use of this data to respond to out-of-control conditions. Superior product quality and efficient manufacturing depends on your laboratory's abilities to handle any number of samples, monitor plant functions, and control the entire laboratory process from start to finish. LABWORKS™ LIMS from PerkinElmer offers you these capabilities, and more. Drawing on nearly 20 years of global experience, dedicated service and the support and strength of our system, we've become one of the leading user-rated LIMS.

Whether it is a new plant system, or a replacement of a previous LIMS, the combination of LABWORKS LIMS' comprehensive functionality and our global team deliver solutions faster with implementation, systems integration, data migration and post-implementation support. Rapid implementation provides you with a faster return on your investment. You can start small and evolve the system as your needs grow. Or start with a larger system and migrate to new product releases over time.

Other capabilities expand your lab

When the need arises for other related analyses, such as fermentation optimization, PerkinElmer offers analytical techniques such as high performance liquid chromatography to help. Thermal analysis techniques are also available to expand the flexibility of the laboratory for a wide range of potential analyses.

Expert, end-to-end service and support

PerkinElmer manufactures and supports the broadest range of instruments, reagents and consumables in the industry. With over 60 years of experience, our knowledge, skills and expertise are unparalleled. We have the largest and most experienced service force in the industry, so you can count on us to be there when you need us. Our 1200 factory-trained and certified engineers have an average 15 years of experience maintaining leading-edge scientific equipment, including preventative maintenance, validation support, from sample handling through data handling.

PerkinElmer Life and Analytical Sciences
710 Bridgeport Avenue
Shelton, CT 06484-4794 USA
Phone: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com

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