

Measure Water Content in Biodiesel Fuels Efficient, reliable and rapid moisture determination using **HYDRANAL**[®] reagents

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Introduction

Escalating oil prices, concerns over its reliable supply and the persistent environmental problems associated with the extraction, production, transport, refinement and combustion of oil and its byproducts have driven research into alternate fuel sources. In the last decade, there has been increased interest in biodiesel, which is derived from renewable sources, such as vegetable oils and animal fats, and conforms to ASTM D6751 and EN-14214 specifications for use in diesel engines. Sigma-Aldrich has recently introduced a number of biodiesel standards for EN 14105 and ASTM D6584 (1).

One practical problem with biodiesel is its hydrophilicity. Some of the water is derived from processing, while some comes from condensation within the storage tank. The presence of water in biodiesel poses a problem for a number of reasons:

- Water reduces the heat of combustion. This means more smoke, harder starting and less power.
- Water will corrode vital fuel system components, like fuel pumps, injector pumps, fuel lines, etc.
- As water approaches 0 °C (32 °F), it begins to form ice crystals. These crystals provide sites of nucleation and accelerate the gelling of the residual fuel.
- Water is required for the growth of most microbes. Biodiesel is an ideal nutrient base for microbes and the presence of water accelerates the growth of microbe colonies, which can clog fuel systems. Biodiesel users who have heated fuel tanks face a year-round microbial growth problem.

Water content in biodiesel can be determined reliably and reproducibly with Karl Fischer titration using **HYDRANAL**[®] reagents (2), as described in this article.

Volumetric Titration

In general, we use **HYDRANAL**[®] Composite 2 as a titration agent. Ethanol-based, non-toxic **HYDRANAL**[®] CompoSolver E (30 mL) is placed in the titration vessel and titrated to dryness with **HYDRANAL**[®] Composite 2. The biodiesel sample (5 mL), precisely measured using differential weighing, is injected into the titration vessel and titrated.

HYDRANAL[®] CompoSolver E can be replaced with **HYDRANAL**[®] LipoSolver CM, which contains chloroform as a solubilizing agent, or **HYDRANAL**[®] LipoSolver MH, which contains 1-hexanol, or **HYDRANAL**[®] Methanol Rapid.

Coulometric Titration

DIN EN 14214/ISO 12937 states that water determination in biodiesel should be carried out by coulometric KF titration method. The coulometric procedure is significantly more sensitive than the volumetric titration. Biodiesel components contain double bonds that can react with iodine, leading to erroneously high results. We observed a small tendency toward this side reaction, but not enough to interfere with the analysis. Falsely high results are evident by extremely fading end points, a typical sign of the side reaction.

We also tested various reagents in cells with and without a diaphragm for coulometric determination of water content. A volume of 5 mL of biodiesel was selected as a single injection in each case, always weighed using the differential weighing method. The precision of the sample manipulation and the coulometric cell can be tested by means of **HYDRANAL**[®] Water Standard 0.10.

Procedure: Coulometry with diaphragm

HYDRANAL[®] Coulomat CG (5 mL) is placed in the cathode chamber of a coulometric cell and approximately 100 mL **HYDRANAL**[®] Coulomat Oil is placed in the anode chamber up to the same level. The coulometer is switched on, and the cell is automatically titrated to dryness. When the drift stabilized at < 10 µg/min, a 5 mL sample that has been precisely measured using differential weighing is injected.

Procedure: Coulometry without diaphragm

This titration follows the same procedure as for coulometry with a diaphragm, except **HYDRANAL®** Coulomat AG-H replaces **HYDRANAL®** Coulomat CG.

Determining the water content using the Karl Fischer oven

Using a KF oven, the biodiesel sample was gradually heated from 50°C to 250°C to test the characteristics of the sample. The temperature ramp indicated that the water was already released by the time the oven reached 80°C. At approximately 120°C, a slight side reaction occurs. At approximately 190°C the sample emits smoke and decomposes. The temperature profile suggested that 100°C is suitable for evaporation of the biodiesel sample.

Determining the water content using the Karl Fischer oven

HYDRANAL® Coulomat CG (5 mL) is placed in the cathode chamber of a coulometric cell with diaphragm

and approximately 100 mL **HYDRANAL®** Coulomat AG Oven is placed in the anode chamber up to the same level. A 4 mL biodiesel sample, evaporated as previously described above, is titrated in this manner.

The cell without a diaphragm requires only 100 mL **HYDRANAL®** Coulomat AG Oven. **HYDRANAL®** Molecular Sieve 0.3 nm is well suited as a drying medium for the carrier gas. **HYDRANAL®** Coulomat AG Oven can also be replaced with **HYDRANAL®** Coulomat AG or **HYDRANAL®** Coulomat AD.

References

- [1] Analytix Issue 4-2005; www.sigma-aldrich.com/analytix
[2] Laboratory Application L 546*

*** Laboratory Applications**

Please contact our **HYDRANAL®** Laboratories (hhoffman@europe.sial.com). We will be glad to send you our Laboratory Reports by fax or e-mail. You can also find the full list on our website www.sigmaaldrich.com/hydranal.

Product Listing Selected **HYDRANAL®** Products (see www.sigma-aldrich.com/hydranal for the complete list)

Cat. No.	Brand	Product	Used as...
34806	Riedel-de Haën	HYDRANAL® Composite 2	One component reagent, titre: 1 mL ~ 2 mg water
37855	Riedel-de Haën	HYDRANAL® LipoSolver CM	To use with HYDRANAL® Composite for titration of non-polar substances, fats and oils
37856	Riedel-de Haën	HYDRANAL® LipoSolver MH	To use with HYDRANAL® Composite for titration of non-polar substances, fats and oils
34734	Riedel-de Haën	HYDRANAL® CompoSolver E	Methanol-free working medium
37817	Riedel-de Haën	HYDRANAL® Methanol Rapid	Solvent for a fast Karl-Fischer titration, max. 0.02% water
34807	Riedel-de Haën	HYDRANAL® Coulomat A	Anolyte for cells with diaphragm, reagent contains chloroform
34868	Riedel-de Haën	HYDRANAL® Coulomat Oil	Anolyte for titration of oils
34843	Riedel-de Haën	HYDRANAL® Coulomat AG-H	Anolyte for titration of long-chained hydrocarbons free of halogenated hydrocarbons
34739	Riedel-de Haën	HYDRANAL® Coulomat AG Oven	Anolyte for determination with KF-oven
34840	Riedel-de Haën	HYDRANAL® Coulomat CG	Catholyte, free of halogenated hydrocarbons, 25 mL bottle resp. 10 x 5 mL ampoules
34847	Riedel-de Haën	HYDRANAL® Water Standard 0.10	1 g contains 0.10 mg = 0.01 % water, contains 10 glass ampoules of 4 mL, traceable to NIST SRM 2890
34241	Riedel-de Haën	HYDRANAL® Molecular sieve 0.3 nm	Drying agent for Karl Fischer applications

**Technical Support**

If you have further questions concerning **HYDRANAL®**, its use and applications, please contact us at:

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