SIGMA-ALDRICH

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Determining the water content in Biodiesel

We tested the water content of biodiesel extensively according to volumetric and coulometric procedures. In addition, the sample was examined using the KF oven together with a coulometer.

Biodiesel can contain substances of different chain lengths. The biodiesel we examined was largely dissolved in methanol, although others do not dissolve. Consequently, we also analysed the biodiesel in reagents that contain dissolution agents. Even though they do not dissolve the biodiesel, they need to disperse it finely so that the water content can be extracted rapidly.

Volumetric titration

In general, we used **HYDRANAL®**-Composite 2 as a titration agent. In each case, 30 ml of the tested media was placed in the titration vessel (see below).
An amount of 5 ml of Biodiesel, precisely measured using differential weighing, was always injected.

1. In **HYDRANAL®**-LipoSolver CM (contains chloroform as solubilizer)
we found 296 ppm, 298 ppm and 301 ppm H_2O (clarity after dissolution in all samples).

2. In **HYDRANAL®**-LipoSolver MH (contains 1-hexanol as solubilizer)
we found 298 ppm, 301 ppm and 302 ppm H_2O (clarity after dissolution in all samples).

3. In **HYDRANAL®**-Methanol Rapid
we found 295 ppm, 296 ppm and 296 ppm H_2O (almost dissolved, light cloudiness).

4. In **HYDRANAL®**-Solvent
we found 299 ppm, 298 ppm and 299 ppm H_2O (cloudiness).

5. In **HYDRANAL®**-CompoSolver E (ethanol-based, non-toxic)
we found 306 ppm, 310 ppm and 313 ppm H_2O (clarity after dissolution).

Volumetric procedure

30 ml of one of the above media 1-5is placed in the titration vessel and dry titrated with **HYDRANAL®**-Composite 2.

Approximately 5 ml of the sample, weighed precisely using differential weighing is then injected, and the water content is titrated with **HYDRANAL®**-Composite 2.

Coulometric determination

The coulometric procedure is significantly more sensitive than the volumetric titration. Biodiesel contains double bindings that can react with iodine. In this sample, we observed a small tendency to this side reaction; the results were not contaminated by this. However, if a sample shows an extremely fading end point setting (a typical sign of a side reaction), the water content found can be correspondingly too high.

We also tested various reagents in the cell 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 differential weighing.

Cell with diaphragm

1. **HYDRANAL®**-Coulomat Oil (contains chloroform + xylene besides methanol)
We injected 15 samples = 50 ml and found 290 ppm H_2O, std.dev. 3.2 ppm
Exsolution after switching off the magnetic stirrer.

2. **HYDRANAL®**-Coulomat A (contains chloroform besides methanol)
We injected 11 samples = 30 ml and found 298 ppm H_2O std.dev. 5.8 ppm.
Dissolution of 15 ml occurred; exsolution after switching off the magnetic stirrer.

Cell without diaphragm

HYDRANAL®-Coulomat AG-H (contains 1-pentanol besides methanol)
We injected 9 samples = 24 ml and found 297 ppm H_2O std. dev. 2.6 ppm.
The conductivity limit was reached after 24 ml of the sample.
The samples were all dissolved.
This anolyte can also be used in the cell with a diaphragm.

Procedure: Coulometry with diaphragm

5 ml **HYDRANAL®**-Coulomat CG 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 dry titrated. When the drift has stabilised at < 10 µg/min, a 5 ml sample that has been precisely measured using differential weighing is injected.

Procedure: Coulometry without diaphragm

HYDRANAL®-Coulomat AG-H is placed in the anode chamber of the coulometric cell.

The coulometer is switched on, and the cell is automatically dry titrated. When the drift has stabilised at < 10 µg/min, a 5 ml sample that has been precisely measured using differential weighing is injected.

The precision of the sample manipulation and the coulometric cell can be tested by means of **HYDRANAL®**-Water Standard 0.10.

Determining the water content using the Karl Fischer oven

The biodiesel 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 at approximately 80°C; at approximately 120°C a light side reaction occurs; at approximately 190°C the sample emits smoke and distils.

Approximately 4 ml of the biodiesel was precisely weighed in each case and evaporated at 100°C.

We found 291 ppm, 290 ppm and 292 ppm H_2O.

Determining the water content using the Karl Fischer oven

5 ml **HYDRANAL®**-Coulomat CG 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.

The cell without a diaphragm requires only 100 ml **HYDRANAL®**-Coulomat AG Oven.

The machine is switched on, and automatically dry titrates. If the drift is downwards (< 10 µg H_2O/min) and stable, the carrier gas is connected. If approximately the same original stable drift value is obtained together with the carrier gas, the sample can be evaporated. **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.

Results

Biodiesel can be determined in a reliable and extremely reproducible manner by various procedures.

We found:

Volumetric titration	296 ppm - 313 ppm
Coulometric determination	290 ppm - 298 ppm
Karl Fischer oven with coulometer	290 ppm - 292 ppm

Reagents

34806 **HYDRANAL®**-Composite2	34807 **HYDRANAL®**-Coulomat A
37855 **HYDRANAL®**-LipoSolver CM	34868 **HYDRANAL®**-Coulomat Oil
37856 **HYDRANAL®**-LipoSolver MH	34843 **HYDRANAL®**-Coulomat AG-H
37817 **HYDRANAL®**-Methanol Rapid	34739 **HYDRANAL®**-Coulomat AG Oven
34800 **HYDRANAL®**-Solvent	34840 **HYDRANAL®**-Coulomat CG
34734 **HYDRANAL®**-CompoSolver E	34847 **HYDRANAL®**-Water Standard 0.10
	34241 **HYDRANAL®**-Molecular Sieve 0.3 nm

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