Water content determination in biodiesel according to EN ISO 12937

R. Schlink[1], B. Faas[2]

Metrohm
Ion analysis

Karl Fischer

Introduction

The presence of water in biodiesel reduces the calorific value and enhances corrosion. Moreover, water promotes the growth of microorganisms and increases the probability that oxidation products are formed during long-term storage. These oxidation products can cause disturbances in the injection system and in the engine itself. In view of this, the EN 14214 standard specifies a maximum water content of 500 ppm for biodiesel.

EN ISO 12937 prescribes coulometric Karl Fischer titration (KFT) for determining the water content of engine fuels. In most cases the sample can be directly injected into the KF solution. In order to improve the solubility of the samples, xylene is added to the KF reagent. In this work, we checked if some commercially available KF reagents that contain solubilizers can be used. Additionally, we determined the water content by an automated KF pipetting system and compared the results to those obtained by manual KFT.

Many biodiesel fuels contain additives or impurities that can undergo side reactions during coulometric KF titration. In these cases the fuel should not be injected directly into the KF solution. Instead, the sample's water content has to be driven off at approx. 120 °C using a KF oven and transferred to the KF coulometer titration cell in a flow of carrier gas. This process can also be fully automated with the 774 Oven Sample Processor.

Repeatability r according to EN ISO 12937

According to EN ISO 12937, the test results must meet the following requirements regarding repeatability:

The difference between two results, obtained by the same person under identical test conditions, may exceed the following value r for the repeatability only once in 20 cases:

$$r = 0.01874 \cdot \sqrt{x},$$

where x is the mean value of all test results given as a mass fraction in percent rounded off to 0.001%.

Instrumentation

Direct coulometric titration (manual KFT)	Automated KF pipetting system (direct injection)	Oven method
➢ 756 Coulometer	➢ 831 KF Coulometer	➢ 831 KF Coulometer
➢ 728 Magnetic Stirrer	➢ 801 Magnetic Stirrer	➢ 728 Magnetic Stirrer
	➢ 815 USB Robotic Sample Processor	➢ 774 Oven Sample Processor
	➢ 800 Dosino	
	➢ Dosing Unit 10 mL	



Direct coulometric titration

By means of direct coulometric titration the water content of biodiesel sample A (free of admixtures and antioxidants) is calculated for different commercially available KF reagents.

Sample A	Diaphragm[2]	Sample size: Minimum value [mg]	Sample size: Maximum value [mg]	Water content: Minimum value x_{min} [ppm]	Water content: Maximum value x_{max} [ppm]	Water content: Mean value x^1 [ppm]	Water content: RSD [%]	Difference $x_{max} - x_{min}$ [ppm]	Repeatability r [ppm]
Coulomat AG (without solubilizer)	√	1600.4	2800.7	184.9	189.6	187.7	0.8	4.7	25.7
Coulomat AG + Xylene	√	967.1	1969.5	192.8	199.5	196.6	1.1	6.7	26.3
Coulomat AG Oil ($CHCl_3$ + Xylene)	√	1761.2	1858.2	179.4	183.0	181.3	0.7	3.6	25.2
Coulomat A ($CHCl_3$)	√	1339.6	2918.1	188.9	194.3	191.7	1.0	5.4	25.9
Coulomat AG-H (long-chain alcohol)	–	1738.0	1763.1	186.1	191.5	189.1	0.9	5.4	25.8

[1]mean of ten determinations; [2] – = cell without diaphragm, √ = cell with diaphragm; 1 000 000 ppm = 100% (187.7 ppm = 0.019%)

Irrespective of the added KF reagent, all results are in the same ppm range. However, the presence of admixtures in the biodiesel requires the addition of a solubilizer. The numerical values for the difference x_{max}-x_{min} are much smaller than those for the repeatability r. This clearly shows that direct KFT provides a far better repeatability r for the water content in biodiesel than is required by EN ISO 12937.

Automated KF pipetting system

High sample throughputs should be handled by automation. An automated pipetting system transfers biodiesel sample B (stabilized with antioxidants) to the coulometric cell.

Sample B	Manual KFT	Automated KF pipetting system
Mean value water content x^1 [ppm]	228.5	223.5
Relative standard deviation [%]	0.41	0.40
$\frac{x \cdot 100}{228.45}$ [%]	100	98
Maximum value x_{max} [ppm]	229.3	224.3
Minimum value x_{min} [ppm]	226.8	221.8
Difference $x_{max} - x_{min}$ [ppm]	2.5	2.5
Repeatability r	28.3	28.0

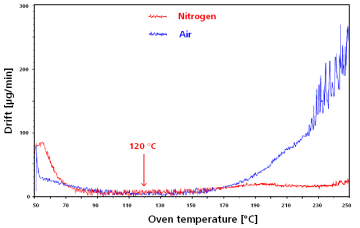
[1]mean of six determinations

Both manual direct injection KFT (228.5 ppm) and the automated KF pipetting system (223.5 ppm) yielded comparable water contents. Moreover the results comply with EN ISO 12937.

Oven method

In order to exclude reactions of additives with the iodine, the water content of biodiesel sample B is determined by the KF oven method. The optimum oven temperature should ensure complete water extraction in a reasonable time while excluding side reactions. It is determined by means of a so-called heating curve that is recorded at a heating rate of 2 °C/min over the temperature range 50 to 250 °C. In the heating curve, the amount of released water per unit time (drift) is plotted as a function of the oven temperature.

- **The biodiesel sample B releases its water content between 50 and 110 °C.**
- **Side reactions start at about 150 °C. They are more pronounced when air is used as carrier gas.**



Based on the knowledge obtained from the heating curve, the following water determinations were performed at an oven temperature of 120 °C.

Sample A	Diaphragm[2]	Sample size: Minimum value [mg]	Sample size: Maximum value [mg]	Water content: Minimum value x_{min} [ppm]	Water content: Maximum value x_{max} [ppm]	Water content: Mean value x^1 [ppm]	Water content: RSD [%]	Difference $x_{max} - x_{min}$ [ppm]	Repeatability r [ppm]
Coulomat AG Oven	–	1694.7	2060.7	177.6	188.4	183.9	1.9	10.8	25.4

[1]mean of ten determinations; [2] – = cell without diaphragm, √ = cell with diaphragm; 1 000 000 ppm = 100% (183.9 ppm = 0.018%)

The results of the oven method comply with the requirements of EN ISO 12937. The small variation between the results obtained by direct coulometric injection (181.3…196.6 ppm) and those by the oven method (183.9 ppm) indicates that the investigated biodiesel sample A contained no additives that reacted with the iodine, as these would have interfered with the direct injections.

Summary

The higher the water content in biodiesel, the lower is its stability. Therefore EN 14214 limits the water content of fatty acid methyl esters to 500 ppm. Two biodiesel samples were analyzed, one with (sample B) and one without (sample A) antioxidants and admixtures. Using different solubilizers, the water content of biodiesel sample A was compared with that obtained by the Karl Fischer oven method. The biodiesel contamination with water was determined for sample B by direct coulometric Karl Fischer Titration (KFT) and the automated KF pipetting system.

Both the direct injection methods, utilizing different solvents as solubilizers, and the oven method yielded comparable water contents for the investigated biodiesel sample A (181.3…196.6 ppm). The good agreement between the results of direct injection and the oven method points to the fact that the investigated biodiesel sample contained no interfering additives, as these would have reacted in the direct titrations. However, in case that some additives undergo side reactions, the KF oven method offers a largely matrix-independent solution as only the water of the sample is transferred to the titration cell of the KF Coulometer. Accordingly, the water content for sample B, determined by the KF Pipetting system (223.5 ppm) agreed well with that obtained by manual KFT (228.5 ppm).

All three tested methods, i.e. the direct coulometric titration, the automated KF pipetting system and the oven method are ideally suited for the determination of the water content in biodiesel and provide a far better repeatability r for the water content in biodiesel than is required by EN ISO 12937.

Download a copy of this poster from http://www.metrohm.com/com/Applications (search for 8.000.6077EN).

[1] Metrohm AG, CH-9101 Herisau/Switzerland, res@metrohm.com, phone +41 71 353 86 64
[2] Deutsche Metrohm GmbH & Co. KG, D-70794 Filderstadt/Germany