Titrimetric analysis of biofuels

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Metrohm
Ion analysis

Titration

Summary

The DIN EN 14214 biodiesel standard stipulates a non-aqueous potentiometric acid-base titration for determining the acid number and a redox titration with sodium thiosulfate solution for the determination of the iodine number. While in the first case the equivalence point is detected by the Solvotrode, the iodine number is determined using a Pt Titrode. Both methods are very user-friendly and characterized by high accuracy and precision. With an acid number of 0.202 mg/g and a iodine number of 114.4 g I_2/100 g, the investigated biodiesel sample complies with the limits of 0.5 mg/g and 120 g I_2/100g stipulated in DIN EN 14214.

According to ASTM D 4806, potentiometric titration of total sulfate in bioethanol with lead nitrate can be performed using a Pb-selective working electrode and a double-junction Ag/AgCl or a glassy-carbon-rod reference electrode. Although both reference electrodes show comparable recovery rates, the latter needs lower maintenance. For both electrodes the ideal operating range is between 1 and 20 ppm sulfate. Corresponding recovery rates are 98…109%. Increasing the sulfate standard and the perchloric acid content in commercial bioethanol blends (E85) allows to monitor sulfate contents in the sub-ppm range.

Introduction

The interest in biofuels obtained from renewable vegetable sources has greatly increased in recent years. The reasons are the increasing demand for mineral oil as well as the environmental problems linked with burning fossil fuels. In order to avoid disturbances in the injection system and in the engine itself, vehicle and biofuel manufacturers have developed quality standards that define testing methods and specifications for biofuels. While there are two major biodiesel standards, the European EN 14214 and the American ASTM D 6751, there currently exists only one major bioethanol standard, the ASTM D 4806. Its European equivalent, the EN 15376, is currently under development.

The determination of the water content of biogenic engine fuels is beyond the scope of this work and is presented under http://products.metrohm.com (search for 8.000.6030EN).

Acid number in biodiesel according to EN 14104

The acid number is a sum parameter comprising all acidic components; it serves as a measure for the long-term stability and corrosiveness of the biofuel. The smaller the value, the higher the quality. Standard EN 14104 in DIN EN 14214 stipulates a non-aqueous potentiometric acid-base titration for determining the acid number.

Iodine number in biodiesel according to EN 14111

The iodine number is a measure for the number of double bonds in a sample. It specifies the amount of iodine in g that are consumed by 100 g of the biodiesel sample under the given conditions. The determination of the iodine number by redox titration with a solution of sodium thiosulfate is described by the European standard EN 14111.

Sulfate content in bioethanol according to ASTM D 7318

Potentiometric titration with lead nitrate is a proven method for sulfate determination, a Pb ISE serving as the indicator electrode. The latter detects the first excess of lead ions at the equivalence point.

Acid number in biodiesel (EN 14104)

Between 14 and 15 g of the biodiesel sample are dissolved in 50 mL of a bioethanol/diethyl ether mixture (1:1). The titrant is an alcoholic solution of potassium hydroxide (0.1 mol/L). After each titration the Solvotrode is thoroughly rinsed with isopropyl alcohol. The regeneration of the membrane is achieved by immersing the electrode in water for at least three minutes.

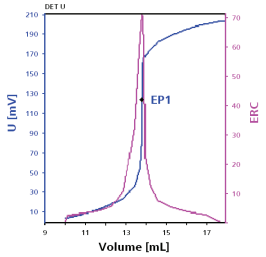
	Titer	Acid number
Number of determinations n	3	9
Mean value	0.987	0.202 mg/g
Standard deviation	0.003	0.002 mg/g
Relative standard deviation	0.34%	0.94%

The acid number determined in the biodiesel sample, in terms of mg KOH per g biodiesel, is 0.202 mg/g. This value complies with the requirements of ASTM D 6751 and EN 14214, which both stipulate a maximal acid number of 0.50 mg/g.

Iodine number in biodiesel (EN 14111)

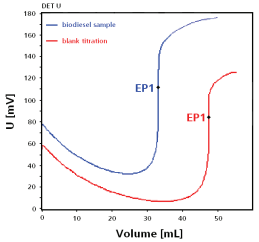
For the titer determination 50 mg potassium iodate, oven-dried overnight, is dissolved in 80 mL distilled water. After the addition of approximately 1 g of potassium iodide and 10 mL of sulfuric acid, the released elemental iodine is titrated with 0.1 mol/L sodium thiosulfate solution. Potentiometric endpoint detection occurs with a Pt Titrode.

Determinations n	Titer
1	1.0155
2	1.0188
3	1.0210
Mean value	1.0184
Standard deviation	0.0027
Relative standard deviation	0.27%



0.15 g of the biodiesel sample is dissolved in 20 mL glacial acetic acid and treated with 25 mL Wijs reagent. After 5 minutes, 15 mL potassium iodide is added. The released elemental iodine is then titrated with 0.1 mol/L sodium thiosulfate solution up to the first end point.

	Blank	Biodiesel
Number of determinations n	3	7
Mean value thiosulfate consumption [mL]	47.71	33.79
Iodine number [g iodine/100 g sample]	—	114.40
Standard deviation	—	0.50
Relative standard deviation [%]	—	0.44

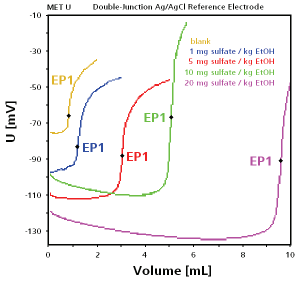


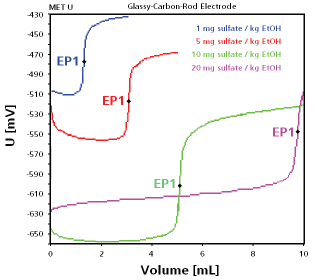
The investigated biodiesel sample has a iodine value of 114.4 and thus meets the requirements of EN 14111, which allows a maximal value of 120 g iodine per 100 g sample.

Sulfate content in bioethanol (ASTM D 7318)

ASTM D 7318 in ASTM D 4806 prescribes a potentiometric titration procedure for the determination of sulfate.

100 g of the bioethanol sample is spiked with known amounts of a sulfate standard. After the addition of 1 mL of 0.1 mol/L perchloric acid the sulfate is precipitated with a lead nitrate solution. The Pb-selective electrode detects the first excess of lead ions at the equivalence point. A double-junction Ag/AgCl or a glassy-carbon-rod electrode are used as the reference electrode.





Conc.	Double-Junction Ag/AgCl Reference Electrode				Glassy-Carbon-Rod Electrode			
	Sulfate conc.[a]	RSD[b]	n[c]	Recovery rate	Sulfate conc.[a]	RSD[b]	n[c]	Recovery rate
[ppm]	[ppm]	[%]		[%]	[ppm]	[%]		[%]
0.998	0.978	0.81	3	98.0	1.063	1.46	3	106.5
4.989	5.229	0.41	4	104.8	5.268	0.23	3	105.6
9.978	10.047	0.52	4	100.7	10.063	0.24	3	100.9
19.965	21.627	1.08	5	108.3	21.735	0.75	4	108.9

[a]sulfate concentrations determined by potentiometric titration, [b]relative standard deviation, [c]number of determinations

While sulfate concentrations between 5 and 10 ppm result in recovery rates of 100.7…105.6%, sulfate contents of 1 and 20 ppm provide recovery rates of 98.0…106.5% and 108.3…108.9%, respectively.

Sulfate content of an E85 bioethanol sample

The low sulfate content in commercial bioethanol fuel blends results in a marginal consumption of lead nitrate, thus impairing the standard deviation. Moreover, a possible lead carbonate formation and weighing errors from evaporation losses falsify the results. In the following, we evaluate the influence of increased sulfate standard and perchloric acid addition on the method precision.

Bioethanol sample E 85	n[a]	Concentration [mg sulfate/kg sample]	RSD[b] [%]
+ 0.2 mL sulfate standard (blank) + 1.0 mL perchloric acid (0.1 mol/L)	3	0.348	4.81
+ 0.4 mL sulfate standard (blank) + 2.0 mL perchloric acid (0.1 mol/L)	3	2.087	0.27

[a]number of titrimetric analyses, [b]relative standard deviation

The precision of the determinations is significantly improved by dublicating the content of perchloric acid and sulfate standard.

The observed sulfate concentration of 2.087 ppm is below the limit of 4 pm stipulated by ASTM D 4806.

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