



Infoletter: Tolerances in analytic testing methods

The quality of biodiesel is examined by producers and customers on the basis of standardized analysis methods in accordance with the norm specification for biodiesel DIN EN 14214.

The following table shows the repeatability and reproducibility for test methods as specified in CEN round robin tests.

What does repeatability (r) mean?

Example: A laboratory technician determines the flash point in a biodiesel sample twice consecutively using the same analysis apparatus. He then compares the results. If the difference is less than 1.9°C then the measurement is in order. If the difference is greater however, he must look for the error in the sample or in the way the measurement was carried out.

Parameter	Method	Unit	Repeatability r	Reproducibility R
Ester content	DIN EN 14103	% (m/m)	1,6	3,1
Density at 15 °C	DIN EN ISO 12185	kg/m ³	0,4	1,5
Viscosity at 40 °C	DIN EN ISO 3104	mm ² /s	0,0011x	0,018x
Flash point	ISO/DIS 3679	°C	1,9	15
CFPP at -20 °C	DIN EN 116	°C	1	4,7
Sulfur content	EN ISO 20846	mg/kg	0,0285x + 2	0,1088x+2
Sulfur content	EN ISO 20884	mg/kg	0,026x + 1,356	0,0567x + 1,616
Carbon residue	DIN EN ISO 10370	% (m/m)	0,019	0,077
Cetane number	ISO DIS 5165	-	2,4	5
Water content	DIN EN ISO 12937	% (m/m)	0,01874x ^{0,5}	0,06877x ^{0,5}
Total contamination	EN 12662	mg/kg	2,24	13,6
Oxidation stability	DIN EN 14112	h	0,09x + 0,16	0,25x + 0,23
Acid number	DIN EN 14104	mg KOH/g	0,02	0,06
Methanol content	DIN EN 14110	% (m/m)	0,056x + 0,001	0,221x + 0,003
Free glycerol	DIN EN 14105	% (m/m)	0,0538x + 0,0014	0,5983x + 0,003
Monoglyceride content		% (m/m)	0,119x+0,004	0,124x+0,133
Diglyceride content		% (m/m)	0,06x+0,004	0,192x+0,025
Triglyceride content		% (m/m)	0,1565x+0,004	0,2099x+0,0641
Total glycerol		% (m/m)	0,0687x+0,004	0,4472x-0,01
Iodine value	DIN EN 14111	g lod/100g	3	5
Phosphorous content	DIN EN 14107	mg/kg	0,6	0,192x + 0,025
Metals I (Na + K)	prEN 14538	mg/kg	0,002x + 0,193	0,191x + 0,941
Metals II (Ca + Mg)	prEN 14538	mg/kg	0,0023x + 0,271	0,149x + 0,271

What does reproducibility (R) mean?

Example: A fuel producer has his biodiesel sample from the first example examined in addition externally by another laboratory. His own results and those from the external laboratory may then differ by 15°C and therefore still lie within the precision requirements for the test method.

A further example

If, for example, the monoglyceride content of the production charge is examined in a laboratory and the result is 0.65 % (m/m), then this result has a measurement uncertainty of:

$$0.199 * 0.65 + 0.004 = 0.081 \% \text{ (m/m)}.$$

The own production charge therefore has a monoglyceride content of 0.65 +/- 0.081 % (m/m).

If the sample is then tested again externally, the fluctuation range for the results, when all those involved measure strictly in accordance with the norm is:

$$0.124 * 0.65 + 0.133 = 0.221 \% \text{ (m/m)}$$

If we assume that a customer buys this charge of biodiesel for which the producer has stated monoglyceride of 0.65 % (m/m) and then has this tested by an external laboratory, he could receive values between 0.429 and 0.871 % (m/m).

For a producer this means that he must incorporate a safety factor in his method.

Observance of a limiting value with 95% certainty is obtained with the following limit in production:

$$\text{Limit value of production} = \text{upper limiting value} - 0.59 * R$$

For the example with monoglyceride this means:

$$\begin{aligned} \text{Limit value of production} &= 0.8 - 0.59 * 0.232 \\ &= 0.66 \% \text{ (m/m)} \end{aligned}$$

The same measurement value uncertainty statistics are valid however for a purchaser of biodiesel.

For him applies:

$$\begin{aligned} \text{Limit value for the acceptance of a consignment} \\ &= \text{upper limiting value} + 0.59 * R \end{aligned}$$

In the example given therefore:

$$\begin{aligned} \text{Limiting value for the acceptance} \\ &= 0.8 + 0.59 * 0.232 = 0.94 \% \text{ (m/m)} \end{aligned}$$

The measurement uncertainty has a particularly great effect on the limiting value for glycerin and glyceride and also the ester content and the overall pollution. Here improvements in analysis methods are needed.