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CERTIFICATION REPORT

The certification of the cold filter plugging point (CFPP) and cloud point (CP) in automotive diesel fuel containing a volume fraction of 7 % biodiesel: ERM®- EF004

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Abstract

This report describes the production of ERM®-EF004, which is an automotive diesel fuel material containing a volume fraction of 7 % fatty acid methyl ester (biodiesel) certified for the cold filter plugging point and the cloud point. This material was produced following ISO Guide 34:2009 and is certified in accordance with ISO Guide 35:2006.
The material is an automotive diesel fuel containing a volume fraction of approximately 7 % biodiesel that is based on rapeseed oil fatty acid methyl ester with the addition of 1 g/kg antioxidant (butylhydroxytoluene). It was provided by a producer in Germany. The material was filled in amber glass ampoules. Between unit-homogeneity was quantified and stability during dispatch and storage were assessed in accordance with ISO Guide 35:2006. Within-unit homogeneity was not quantified as the minimum sample intake is defined by the required sample volume stipulated in the respective documentary standard and comprises almost the whole volume of the two ampoules of every unit.
The material was characterised by an interlaboratory comparison of laboratories of demonstrated competence and adhering to ISO/IEC 17025:2005). Technically invalid results were removed but no outlier was eliminated on statistical grounds only.
Uncertainties of the certified values were calculated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM) and include uncertainties related to possible inhomogeneity, instability and characterisation.
The material is intended for quality control and assessment of method performance. As with any reference material, it can be used for establishing control charts or validation studies. The certified reference material (CRM) is available in sets of two amber glass ampoules, each containing 27 mL of automotive diesel fuel material with a volume fraction of 7 % biodiesel closed under argon atmosphere.

CERTIFICATION REPORT

The certification of the cold filter plugging point (CFPP) and cloud point (CP) in automotive diesel fuel containing a volume fraction of 7 % biodiesel: ERM ®- EF004

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Disclaimer

Certain commercial equipment, instruments, and materials are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the European Commission, nor does it imply that the material or equipment is necessarily the best available for the purpose.

Summary

This report describes the production of ERM®-EF004, which is an automotive diesel fuel material containing a volume fraction of 7 % fatty acid methyl ester (biodiesel) certified for the cold filter plugging point and the cloud point. This material was produced following ISO Guide 34:2009 [1] and is certified in accordance with ISO Guide 35:2006 [2].

The material is an automotive diesel fuel containing a volume fraction of approximately 7 % biodiesel that is based on rapeseed oil fatty acid methyl ester with the addition of 1 g/kg antioxidant (butylhydroxytoluene). It was provided by a producer in Germany. The material was filled in amber glass ampoules.

Between unit-homogeneity was quantified and stability during dispatch and storage were assessed in accordance with ISO Guide 35:2006 [2]. Within-unit homogeneity was not quantified as the minimum sample intake is defined by the required sample volume stipulated in the respective documentary standard and comprises almost the whole volume of the two ampoules of every unit.

The material was characterised by an interlaboratory comparison of laboratories of demonstrated competence and adhering to ISO/IEC 17025:2005 [3]). Technically invalid results were removed but no outlier was eliminated on statistical grounds only.

Uncertainties of the certified values were calculated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM) [4] and include uncertainties related to possible inhomogeneity, instability and characterisation.

The material is intended for quality control and assessment of method performance. As with any reference material, it can be used for establishing control charts or validation studies. The certified reference material (CRM) is available in sets of two amber glass ampoules, each containing 27 mL of automotive diesel fuel material with a volume fraction of 7 % biodiesel closed under argon atmosphere.

The following values were assigned:

	Certified value [3] [°C]	Uncertainty [4] [°C]
Cold filter plugging point (CFPP) [1]	-27.9	2.7
Cloud point (CP) [2]	-6.8	0.4

[1] As defined by EN 116:2015 or ASTM D6371-05:2010.

[2] As defined by ISO 3015:1992 (EN 23015:1994) or ASTM D2500-09:2011.

[3] Certified values are values that fulfil the highest standards of accuracy and represent the unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory using one of the above mentioned methods for determination. The certified values and their uncertainties are traceable to the International System of units (SI).

[4] The uncertainty of the certified value is the expanded uncertainty with a coverage factor $k = 2$ corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

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Glossary

ASTM international	ASTM international (formerly American Society for Testing and Materials)
ANOVA	Analysis of variance
b	Slope in the equation of linear regression $y = a + bx$
CEN	European Committee for Standardization
CFPP	Cold filter plugging point
CP	Cloud point
CI	Confidence interval
CRM	Certified reference material
df	Degrees of freedom
EC	European Commission
EN	European norm (standard)
ERM®	Trademark of European Reference Materials
EU	European Union
GUM	Guide to the Expression of Uncertainty in Measurement
ISO	International Organization for Standardization
JRC	Joint Research Centre of the European Commission
k	Coverage factor
m/m	Mass fraction
$MS_{between}$	Mean of squares between-unit from an ANOVA
MS_{within}	Mean of squares within-unit from an ANOVA
n	Number of replicates per unit
QC	Quality control
r	Repeatability limit
R	Reproducibility limit
s	Standard deviation
s_{bb}	Between-unit standard deviation
$s_{between}$	Standard deviation between groups as obtained from ANOVA
SI	International System of Units
s_{meas}	Standard deviation of measurement data
s_r	Repeatability standard deviation
S_R	Reproducibility standard deviation
s_{within}	Standard deviation within groups as obtained from ANOVA
s_{wb}	Within-unit standard deviation

T	Temperature
t	Time
t_i	Time point for each replicate
$t_{\alpha,\,df}$	Critical *t*-value for a *t*-test, with a level of confidence of 1-α and df degrees of freedom
t_{sl}	Proposed shelf life
t_{tt}	Proposed transport time
u	Standard uncertainty
U	Expanded uncertainty
u^*_{bb}	Standard uncertainty related to a maximum between-unit inhomogeneity that could be hidden by intermediate precision
u_{bb}	Standard uncertainty related to a possible between-unit inhomogeneity
u_c	Combined standard uncertainty
u_{char}	Standard uncertainty of the material characterisation
u_{CRM}	Combined standard uncertainty of the certified value
U_{CRM}	Expanded uncertainty of the certified value
u_Δ	Combined standard uncertainty of measurement result and certified value
u_{lts}	Standard uncertainty of the long-term stability
u_{meas}	Standard measurement uncertainty
U_{meas}	Expanded measurement uncertainty
u_{sts}	Standard uncertainty of the short-term stability
α	Significance level
Δ_{meas}	Absolute difference between mean measured value and the certified value
$\nu_{s,meas}$	Degrees of freedom for the determination of the standard deviation s_{meas}
$\nu_{MSwithin}$	Degrees of freedom of MS_{within}
V/V	Volume fraction

1 Introduction

1.1 Background

The Fuel Quality Directive 98/70/EC [5] as amended by Directive 2009/30/EC [6], as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions, sets common fuel quality rules that are an important element for ensuring that air pollutant emissions from vehicles are optimally reduced, a single fuel market is established and vehicles operate correctly everywhere in the European Union.

In 1993 the European Committee for Standardization (CEN) was mandated by the European Commission and the European Free Trade Association [7] to develop a uniform standard that is defining product specifications and measurement methods for automotive diesel fuel, resulting in the documentary European Standard EN 590 [8]. This standard is designed to meet the needs of European business and industry, whilst also taking into account the legitimate concerns of consumers and other stakeholders, and the requirements of relevant European legislation [5, 6]. It is applicable to automotive diesel fuel for use in diesel engine vehicles designed to run on automotive diesel fuel containing a volume fraction of up to 7.0 % fatty acid methyl ester (FAME), so-called 'diesel (B7)'.

Many of the specified parameters in EN 590 [8] rely on "method-specific" data obtained using standardised measurement procedures. Amongst them are the cold flow properties, including cloud point, cold filter plugging point and the pour point. However, the availability and use of these standard methods do not per se guarantee reliable measurement results. It is widely accepted that laboratories need to demonstrate their proficiency in the application of standard methods. ISO/IEC 17025 [3] explicitly states "*The laboratory shall confirm that it can properly operate standard methods before introducing the tests or calibrations. If the standard method changes, the confirmation shall be repeated*". In order to provide the analytical laboratories with the necessary tools for adequate quality assurance and quality control during the analysis of automotive diesel fuels, suitable CRMs are necessary.

ERM-EF004 is certified for the cold filter plugging point (CFPP) and the cloud point (CP). The provision of ERM-EF004 increases the comparability and reliability of measurements between laboratories, allowing laboratories to prove their competences. Other parameters specified in EN 590 [8] are covered by ERM-EF003 [9], certified for the volume fraction of the fatty acid methyl ester content, the mass fraction of mono-aromatic hydrocarbon, di-aromatic hydrocarbon, polycyclic aromatic hydrocarbon, and total aromatic hydrocarbon content, and density, viscosity, and lubricity.

1.2 Choice of the material

EN 590 [8] is applicable to automotive diesel fuel for use in diesel engine vehicles designed to run on automotive diesel fuel containing a volume fraction of up to 7 % fatty acid methyl ester. Hence, the chosen base material is a commercial automotive diesel fuel which was taken directly from the refinery blender unit without containing fatty acid methyl esters. This diesel was blended with biodiesel that is based on rapeseed oil fatty acid methyl ester with the addition of an antioxidant (butylhydroxytoluene), to achieve a volume fraction of 7 % biodiesel. The final blend, i.e. diesel (B7), was provided by a producer in Germany.

1.3 Design of the CRM project

The homogeneity and stability of the material were evaluated through studies involving measurement of the two parameters using the documentary standards EN 116 [10] for CFPP

and ISO 3015 [11] for CP. The certified values were established by an intercomparison of different laboratories using EN 116 [10] and ASTM D6371-05 [12] for CFPP and ISO 3015 [11] (also known as EN 23015 [13]) and ASTM D2500-09 [14] for CP. A closer look at the methods for each parameter reveals that they differ only slightly in some of the specifications of thermometers, but that the specifications for the main steps are the same. Therefore, the methods can be considered equivalent. Moreover, ASTM D6371-05 [12] explicitly states that the method is technically equivalent to EN 116 [10] for CFPP.

2 Participants

2.1 Project management and evaluation

European Commission, Joint Research Centre, Directorate F – Health, Consumers and Reference Materials, Reference Materials Unit, Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM)

2.2 Processing

European Commission, Joint Research Centre, Directorate F – Health, Consumers and Reference Materials, Reference Materials Unit, Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM)

2.3 Homogeneity study

ASG Analytik-Service Gesellschaft mbH, Neusäss, DE
(measurements under the scope of ISO/IEC 17025 accreditation DAkkS D-PL-11334-01-00)

OŰ EESTI KESKKONNAUURINGUTE KESKUS (Estonian Environmental Research Centre), Tallinn, EE
(measurements under the scope of ISO/IEC 17025 accreditation EAK L008)

2.4 Stability study

ASG Analytik-Service Gesellschaft mbH, Neusäss, DE
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2.5 Characterisation

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(measurements partially under the scope of ISO/IEC 17025 accreditation BELAC; No. 105-TEST)

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(measurements under the scope of ISO/IEC 17025 accreditation EAK L008)

SGS Belgium NV, Antwerp, BE
(measurements under the scope of ISO/IEC 17025 accreditation BELAC No. 005-TEST)

SGS ESPAÑOLA DE CONTROL, S.A.U., Barcelona, ES
(measurements under the scope of ISO/IEC 17025 accreditation ENAC 14/LE249 Rev.15)

VÚRUP, a.s., Bratislava, SK
(measurements under the scope of ISO/IEC 17025 accreditation SNAS No. S-119)

3 Material processing and process control

3.1 Origin of the starting material

A commercial mixture of automotive diesel fuel and biodiesel based on rapeseed oil fatty acid methyl ester with the addition of about 1 g/kg of the antioxidant butylhydroxytoluene (supplier information) was selected as base material and provided by ASG Analytik-Service Gesellschaft mbH, Neusäss (DE). Three metal barrels containing in total 300 L of the material were delivered to the JRC at Geel. The compliance of the fuel with EN 590 [8] was verified by analysis of the fuel.

Table 1: Analysis of the starting material

Parameter	Unit	Result	Specification	Test method
Cetane number (DCN)	-	53.1	min. 51	EN 15195 [15]
Cetane Index	-	53.4	min. 46	EN ISO 4264 [16]
Density (15 °C)	[kg/m^3]	837.2	820 - 845	EN ISO 12185 [17]
Polycyclic aromatic hydrocarbon content	[% (m/m)]	2.3	max. 8	EN 12916 [18]
Sulfur content	[mg/kg]	7.7	max. 10	EN ISO 20884 [19]
Flash point	[°C]	74	>55	EN ISO 2719 [20]
Carbon residue (10 % Dist.)	[% (m/m)]	<0.10	max. 0.30	EN ISO 10370 [21]
Ash content (775 °C)	[% (m/m)]	0.005	max. 0.01	EN ISO 6245 [22]
Water content	[mg/kg]	30	max. 200	EN ISO 12937 [23]
Total contamination	[mg/kg]	3	max. 24	EN 12662 [24]
Copper strip corrosion	Korr.Grad	1	1	EN ISO 2160 [25]
Fatty acid methyl ester content	[% (V/V)]	6.8	max. 7	EN 14078 [26]
Oxidation stability	[g/m^3]	15	max. 25	EN ISO 12205 [27]
Filterable insolubles	[g/m^3]	2	-	EN ISO 12205 [27]
Adherent insolubles	[g/m^3]	13	-	EN ISO 12205 [27]
Oxidation stability	[h]	54.4	min. 20	EN 15751 [28]
HFRR (Lubricity)	[µm]	195	max. 460	EN ISO 12156-1 [29]
Kinematic viscosity (40 °C)	[mm^2/s]	2.888	2.00-4.50	EN ISO 3104 [30]
% (V/V) recovery at 250 °C	[% (V/V)]	31.9	<65	EN ISO 3405 [31]
% (V/V) recovery at 350 °C	[% (V/V)]	95.2	min. 85	EN ISO 3405 [31]
95 % (V/V) recovery	[°C]	349.5	max. 360	EN ISO 3405 [31]
CFPP	[°C]	-28	max. 0.5	EN 116 [10]
Manganese content	[mg/L]	<0.5	max. 120	EN 16576 [32]

3.2 Processing

Upon arrival at the JRC at Geel the material was immediately stored at 18 °C in darkness until further treatment. Before ampouling, about 260 L of the material was transferred from the transport drums into a plastic drum over a 125 µm nylon filter to remove residual dust or particles. The material was mixed with an IKA Turbotron (Janke & Kunkel, Staufen, Germany) for 30 minutes and gently bubbled with nitrogen to homogenise the material. The main means of stabilisation were the addition of an antioxidant (butylhydroxytoluene) and application of an inert atmosphere. For the latter, nitrogen was gently bubbled through the material throughout the filling process. To remove most of the oxygen from the amber glass ampoules, they were flushed with argon over the headspace after filling with diesel (B7). Afterwards, the ampoules were flame-sealed. Ampouling was performed on a ROTA automatic ampouling machine, model R910/PA (ROTA Verpackungstechnik GmbH & Co.KG, Wehr, DE). The 30-mL amber glass ampoules were filled with 27 mL of diesel (B7). In total, 4000 ampoules were filled.

The first 2000 ampoules were labelled 0001/A, 0002/A, 0003/A in fill-order. Ampoule 2001 - 4000 were labelled 0001/B, 0002/B, 0003/B in fill-order. Thereafter 2000 sets were made where set 0001 consists of sample 0001/A and 0001/B and so forth. Each unit of the reference material consists of a set of two amber glass ampoules, each containing 27 mL of diesel (B7), placed in a styrofoam box. The contents of the two ampoules must be pooled before performing the measurement. In this report, the term "unit" refers to such a set of two ampoules that are pooled before for analysis.

3.3 Process control

During processing, 16 units were selected, two consecutive ampoules every 500th unit. Water measurements applying coulometric Karl Fischer titration were made on each ampoule. The water content did not show any trend in the filling sequence at a 95 % confidence level and was below 200 mg/kg, which was the predefined quality criterion, indicating that the material was sufficiently homogenous and filled without any trend in fill-order with regard to the water content.

4 Homogeneity

A key requirement for any reference material aliquoted into units is equivalence between those units. In this respect, it is relevant whether the variation between units is significant compared to the uncertainty of the certified value, but it is not relevant if this variation between units is significant compared to the analytical variation. Consequently, ISO Guide 34 [1] requires RM producers to quantify the between unit variation. This aspect is covered in between-unit homogeneity studies.

Within-unit homogeneity is not relevant in this case, as the two ampoules need to be pooled and are used as a whole to allow for one single measurement. For both parameters the minimum sample intake is the required sample volume stipulated in the respective documentary standards.

4.1 Between-unit homogeneity

The between-unit homogeneity was evaluated to ensure that the certified values of the CRM are valid for all units of the material, within the stated uncertainties. The number of units selected for each parameter corresponds to approximately the cube root of the total number of units produced (13 in this case).

The number units were selected using a random stratified sampling scheme covering the whole batch for the between-unit homogeneity test. For this, for each parameter the batch was divided into a number of groups (with a similar number of units) and one unit was selected randomly from each group, and analysed by using the respective standard methods EN 116 [10] for the CFPP and ISO 3015 [11] for the CP.

As different units can only be measured once, the variability between results contains both repeatability and real between-unit variation. To obtain an assessment of the repeatability standard deviation of the laboratory, it was decided to pool 10 units, mix them and perform 10 replicate measurements from the pooled sample, whereas the between-unit measurements were done on the 13 individual units. The principle of the setup is shown in Figure 1.

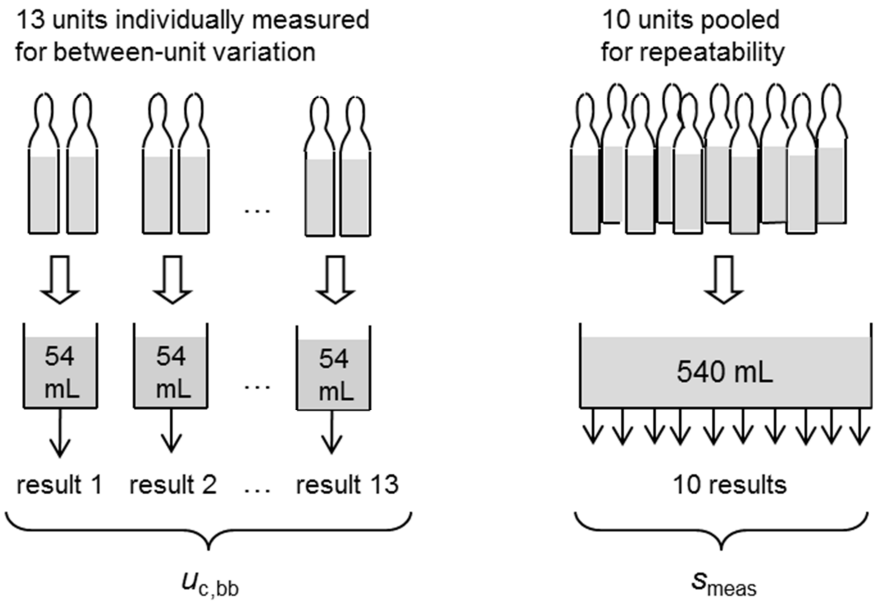

Figure 1: Setup of between-unit homogeneity study

Consequently, for each parameter, 23 units were selected using a random stratified sampling scheme. The measurements for each parameter were performed under intermediate precision conditions (different days). Consequently, day-to-day effects can occur that could mask the between-bottle variation. Therefore, it had to be checked first if there is a significant difference between the day means using ANOVA. Both parameters did not show a significant day-to-day effect. All measurements were done in a randomised manner to be able to separate a potential analytical drift from a trend in the filling sequence. The results are shown as graphs in Annex A.

To check the data for consistency, a test was made whether the results fulfil the reproducibility criteria set in the documentary standards.

According to EN 116 [10], only 1 in 20 pairs of measurements will differ more than 4.7 °C under reproducibility conditions. The 23 measurements spread over three days ranged from -27 °C to -30 °C; hence, none of the pairs differed more than 4.7 °C. Consequently, all measurements fulfilled the quality criteria of the standard and were considered as technically valid.

According to ISO 3015 [11], only 1 in 20 pairs of measurements will differ more than 4 °C under reproducibility conditions. The 23 measurements spread over three days ranged from -4.7 °C to -5.2 °C; hence, none of the pairs differed more than 4 °C. Consequently, all measurements fulfilled the quality criteria of the standard and were considered as technically valid.

Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence. No trends in the filling sequence or the analytical sequence were observed at a 95 % confidence level.

To obtain the standard deviation between units (s_{bb}) the standard deviation from the 13 individual units ($u_{c,bb}$) must be corrected for the pure measurement standard deviation (s_{meas}) coming from the pooled sample as shown in Equation 1 [33].

$$s_{bb} = \sqrt{u_{c,bb}^2 - s_{meas}^2} \qquad \textbf{Equation 1}$$

It should be noted that $u_{c,bb}$ and s_{meas} are estimates of the true standard deviations and are therefore subject to random fluctuations. Therefore, the standard deviation square from individual units can be smaller than the standard deviation squares of pooled units, resulting in negative arguments under the square root used for the estimation of the between-unit variation, whereas the true variation cannot be lower than zero. In this case, u^*_{bb}, the maximum inhomogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [34]. u^*_{bb} is comparable to the limit of quantification of an analytical method, yielding the maximum inhomogeneity that might be undetected by the given study setup. As in both cases $u_{c,bb}$ was smaller than s_{meas} the inhomogeneity that can be hidden by method repeatability is defined as follows in Equation 2, based on the recommendation of Reference [35].

$$u^*_{bb} = s_{meas} \cdot \sqrt[4]{\frac{2}{\nu_{s,meas}}} \qquad \textbf{Equation 2}$$

The resulting values for u^*_{bb} from the above equations were 0.58 °C for CFPP and 0.081 °C for CP, finally taken as uncertainty contribution for between-unit inhomogeneity u_{bb}.

4.2 Within-unit homogeneity and minimum sample intake

The within-unit homogeneity is closely correlated to the minimum sample intake. The minimum sample intake is the minimum amount of sample that is representative for the whole unit and thus should be used in an analysis. Using sample sizes equal or above the minimum sample intake guarantees the certified value within its stated uncertainty. For CFPP and CP the minimum sample intake is the required sample volume stipulated in the respective documentary standards. In both cases, the contents of two ampoules must be pooled for a single analysis.

5 Stability

Time, temperature, light and the presence of oxygen were regarded as the most relevant influences on stability of the material. Principal means of stabilisation were the addition of an antioxidant (butylhydroxytoluene), and creation of an inert atmosphere by flushing argon into the containment just before and after filling, removing the oxygen present, and by bubbling the material with nitrogen throughout the filling. The influence of ultraviolet or visible light was minimised by storing the material in containers which reduces light exposure. In addition, materials are stored in the dark and dispatched in boxes, thus removing any possibility of degradation by light. Therefore, only the influences of time and temperature needed to be investigated.

Stability testing is necessary to establish the conditions for storage (long-term stability) as well as the conditions for dispatch of the materials to the customers (short-term stability). During transport, especially in summer time, temperatures up to 60 °C can be reached and stability under these conditions must be demonstrated, if the samples are to be transported without any additional cooling.

The stability studies were carried out using an isochronous design [36]. In this approach, samples were stored for a particular length of time at different temperature conditions. Afterwards, the samples were moved to conditions where further degradation can be assumed to be negligible (reference conditions). At the end of the isochronous storage, the samples were analysed in the shortest possible time.

5.1 Short-term stability study

For the short-term stability study, samples were stored at -20 °C, 18 °C, 40 °C and 60 °C for 0, 1, 2 and 4 weeks (at each temperature). Storage at 60 °C mimics worst case conditions for transport during hot conditions, whereas storage at -20 °C checks whether first precipitates formed in the sample can be completely re-melted. The 18 °C and 40 °C studies acted as backup for the case that the material would degrade at 60 °C. The reference temperature was set to 4 °C. For both parameters, four units per storage time were selected using a random stratified sampling scheme. Each unit was measured using the standard methods EN 116 [10] for CFPP and ISO 3015 [11] for CP. The measurements were performed under intermediate precision conditions (for each storage temperature spread over 2 working days) due to the long time required for the measurements. All measurements were done in a randomised sequence to differentiate any potential analytical drift from a trend over storage time.

The data were evaluated individually for each temperature. The consistency of the data was checked, by testing whether the results fulfil the reproducibility conditions specified in the standard methods, as explained in section 4.1. The results for the CFPP, ranging from -27 to 30 °C, fulfilled the reproducibility conditions laid down in the documentary standards. The measurements for the CP ranged from -5.9 to -7.0 °C. Hence, none of the pairs differed more than 4 °C. Consequently, all measurements fulfilled the quality criteria of the standard and were considered as technically valid.

In addition, the data were evaluated against storage time, and regression lines of the determined parameters versus time were calculated. The slopes of the regression lines were tested for statistical significance. None of the trends was statistically significant at a 95 % confidence level for any of the temperatures apart from the CFPP tested at 60 °C.

As the measurements for each storage temperature were performed under intermediate precision conditions, it had to be checked too if there is a significant difference between the day means using ANOVA. This is for the simple reason that day-to-day effects can occur that could mask a potential trend. For both parameters for none of the storage temperatures a

significant day-to-day effect was observed, apart from CFPP tested at 18 °C. In this case, a correction was applied by dividing every data point by the respective day mean in order to limit day-to-day effects. In the end, both original data and corrected data did not show a trend at the 95 % confidence level.

The results of the measurements are shown in Annex B. The results of the statistical evaluation of the short-term stability are summarised in Table 2.

Table 2: Results of the short-term stability tests

Parameters	Trends (95 % confidence level)			
	-20 ºC	18 ºC	40 °C	60 °C
CFPP	no	no	no	yes
CP	no	no	no	no

Trends were not statistically significant on a 95 % confidence level for any of the temperatures, except for a negative trend at 60 °C that was observed for the CFPP. At 40 °C none of the parameters showed instability. Consequently, it was decided that the material can be dispatched under ambient conditions. However, a temperature indicator for 40 °C will be added to the shipment, to ensure that the shipping temperatures exceeding this temperature can be detected and remediated.

5.2 Long-term stability study

For the long-term stability study, samples were stored at 18 °C for 0, 4, 8 and 12 months. The reference temperature was set to 4 °C. For both parameters, four units per storage time were selected using a random stratified sampling scheme. Each unit was measured using the standard methods EN 116 [10] for CFPP and ISO 3015 [11] for CP. The measurements were performed under intermediate precision conditions (spread over 2 working days) due to the long time required for the measurements. However, no significant day-to-day effect was observed. All measurements were done in a randomised sequence to differentiate any potential analytical drift from a trend over storage time.

As already explained in section 4.1, the consistency of the data was checked, by testing whether the results fulfil the reproducibility conditions specified in the standard methods. The results for the CFPP, ranging from -27 to -30 °C, fulfilled the reproducibility conditions laid down in the documentary standards. The measurements for the CP ranged from -6.9 to -7.1 °C. Hence, none of the pairs differed more than 4 °C. Consequently, all measurements fulfilled the quality criteria of the standard and were considered as technically valid.

In addition, the data were plotted against storage time and linear regression lines of the determined parameters versus time were calculated. The slopes of the regression lines were tested for statistical significance. No significant trend was detected for both parameters at a 95 % confidence level.

The results of the long-term stability measurements are shown in Annex C. None of the trends was statistically significant on a 99 % confidence level. The material can therefore be stored at 18 ± 5 °C.

5.3 Estimation of uncertainties

Due to the intrinsic variation of measurement results, no study can entirely rule out degradation of materials, even in the absence of statistically significant trends. It is therefore necessary to quantify the potential degradation that could be hidden by the method intermediate precision, i.e. to estimate the uncertainty of stability. This means that, even under ideal conditions, the outcome of a stability study can only be that there is no detectable degradation within an uncertainty to be estimated.

The uncertainties of stability during dispatch and storage were estimated, as described in [35] for each parameter. In this approach, the uncertainty of the linear regression line with a slope of zero was calculated. The uncertainty contributions u_{sts} and u_{lts} were calculated as the product of the chosen transport time/shelf life and the uncertainty of the regression lines as:

$$u_{sts} = \frac{s}{\sqrt{\sum \left(t_i - \bar{t}\right)^2}} \cdot t_{tt} \qquad \textbf{Equation 3}$$

$$u_{lts} = \frac{s}{\sqrt{\sum \left(t_i - \bar{t}\right)^2}} \cdot t_{sl} \qquad \textbf{Equation 4}$$

s standard deviation of all results of the stability study

t_i time elapsed at time point *i*

$\bar{t}$ mean of all t_i

t_{tt} chosen transport time (1 week at 40 ºC)

t_{sl} chosen shelf life (24 months at 18 ºC)

The following uncertainties were estimated:

- u_{sts}, the uncertainty of degradation during dispatch. This was estimated from the 40 °C studies. The uncertainty describes the possible change during a dispatch at 40 °C lasting for one week.
- u_{lts}, the stability during storage. This uncertainty contribution was estimated from the 18 °C studies. The uncertainty contribution describes the possible degradation during 24 months storage at 18 °C.

The results of these evaluations are summarised in Table 3.

Table 3: Uncertainties of stability during dispatch and storage. u_{sts} was calculated for a temperature of 40 °C and 1 week; u_{lts} was calculated for a storage temperature of 18 °C and 24 months

Parameters	u_{sts} [°C]	u_{lts} [°C]
	40 °C	18 °C
Cold filter plugging point	0.14	1.04
Cloud point	0.055	0.088

For the CP no significant degradation during dispatch was observed even at 60 °C. For the CFPP a significant degradation during dispatch at 60 °C was observed but not at 40 °C. Therefore, the material can be transported at ambient conditions. However, a temperature indicator for 40 °C will be added to the shipment, to ensure that the shipping temperatures exceeding this temperature can be detected and remediated.

The material can be stored at 18 ± 5 °C. Stability was confirmed by the outcome of a two year long-term stability study, which was completed just before the release of the material.

After the certification study, the material will be included in the JRC's regular stability monitoring programme, to control its further stability.

6 Characterisation

The material characterisation is the process of determining the property values of a reference material. To make the certified values as widely applicable as possible, it was decided to apply as many technically equivalent methods as possible. Absence of difference between results of these methods would demonstrate the equivalence for this material and make it useful for any of these methods. For that reason, characterisation was performed using the standard methods EN 116:2015 [10] and ASTM D6371-05:2010 [12] for CFPP and ISO 3015:1992 [11] (equivalent to EN 23015:1994 [13]) and ASTM D2500-09:2011 [14] for CP. A closer look at the methods for each parameter reveals that they differ only slightly in some of the specifications of thermometers, but that the specifications for the main steps are the same. Therefore, the methods can be considered equivalent, which was also confirmed by the participating laboratories of the intercomparison study. Moreover, ASTM D6371-05:2010 [12] explicitly states that the method is technically equivalent to EN 116 [10] for CFPP. The equivalence was also demonstrated in previous certification studies for a diesel and a biodiesel material [37, 38].

The characterisation was based on an interlaboratory comparison of expert laboratories, i.e. the properties of the material were determined in different laboratories using the methods mentioned above.

6.1 Selection of participants

For the interlaboratory comparison laboratories could submit more than one dataset. For the CFPP, 13 laboratories were selected that should deliver 18 datasets, whereas for the CP 12 laboratories delivering 19 datasets were chosen. They were selected based on criteria that comprised both technical competence and quality management aspects. Each participant was required to operate a quality system and to deliver documented evidence of its laboratory proficiency for the respective parameters in the field of diesel measurements by submitting results for intercomparison exercises or method validation reports. Having a formal accreditation was not mandatory, but meeting the requirements of ISO/IEC 17025 [3] was obligatory. Where measurements are covered by the scope of accreditation, the accreditation number is stated in the list of participants (Section 2).

6.2 Study setup

For every parameter and method, each laboratory received six units of ERM-EF004 and was requested to provide six independent results, one per unit. The units for material characterisation were selected using a random stratified sampling scheme and covered the whole batch. The measurements had to be spread over at least three days (two units per day) to ensure intermediate precision conditions.

Each participant received samples of ERM-EF002 [38] as a blinded quality control (QC) sample. The results for this sample were used to support the evaluation of the characterisation results.

Laboratories were not requested to give estimations of the expanded uncertainties of the mean value of the six results, as the accuracy of the methods is described in the respective documentary standards. However, all laboratories were asked to follow strictly the standard test method protocols as provided in EN 590 [8].

6.3 Methods used

For the CFPP 13 laboratories used the method EN 116:2015 [10]. Five of them applied additionally the ASTM D6371-05:2010 [12] approach. For the CP 12 labs performed their measurements with ISO 3015:1992 [11] (equivalent to EN 23015:1994 [13]) and 7 of them were additionally using the ASTM D2500-09:2011 [14]. A summary of the individual measurement methods, giving their scopes and principles, is listed in Annex D (Table D1-D4).

6.4 Evaluation of results

The characterisation study resulted in 18 datasets for CFPP and 19 datasets for CP. All individual results of the participants, grouped per parameter are displayed in tabular and graphical form in Annex E.

6.4.1 Technical evaluation

The obtained data were first checked for compliance with the requested analysis protocol and for their validity based on technical reasons. The following criteria were considered during the evaluation:

- strictly follow documentary standard.
- compliance with the analysis protocol: sample preparations and measurements performed on three days.
- method performance,
    - agreement with performance criteria of documentary standards:
        - Datasets were rejected when the absolute difference between two independent test results from two different units exceeded the reproducibility limit (R) as laid down in the documentary standard
    - agreement of the measurement results with the assigned value of the QC sample:
        - Datasets were rejected when the QC results did not agree with the assigned values of ERM-EF002 according to ERM Application Note 1 [39], using for the uncertainty of the measured value the measurement uncertainties (u_{meas}) derived from the respective documentary standards. These documentary standards give information on expected repeatability and reproducibility limits. The absolute difference between two single test results obtained under repeatability conditions can be expected to be less than or equal to the value of r, the repeatability limit, with a certain probability (usually 95 %). A reproducibility limit, *R*, is similarly defined for test results obtained under reproducibility conditions [40]. A repeatability limit is calculated from:

          $r = t \times \sqrt{2} \times s_r$ **Equation 5**

          where *t* (1.96) is the two-tailed Student *t* value at the 95 % confidence level and s_r is the repeatability standard deviation.

          Similarly, the reproducibility limit is calculated from:

          $R = t \times \sqrt{2} \times s_R$ **Equation 6**

          where s_R is the reproducibility standard deviation.

As the standard deviation between laboratories (s_L) is [41]

$$s_L = \sqrt{s_R^2 - s_r^2} \qquad \textbf{Equation 7}$$

and as the expanded measurement uncertainty (U_{meas}) of an average of n measurements is

$$U_{meas} = 2 \cdot \sqrt{s_L^2 + \frac{s_r^2}{n}} \qquad \textbf{Equation 8}$$

expanded measurement uncertainties were estimated for n = 6 replicates. Precision data as laid down in respective documentary standards and estimated expanded measurement uncertainties thereof are summarised in Table D5 of Annex D.

All laboratories complied with the analysis protocol and were strictly following the documentary standards. Based on the above criteria, three datasets were rejected as not technically valid.

Laboratory 3 measuring the CFPP using the ASTM D6371-05 method did not meet the reproducibility limit.

From laboratory 7 for CFPP both datasets obtained by EN 116 and ASTM D6371-05 were not accepted, as the obtained datasets did not meet the performance criteria of the methods when compared to each other. The ASTM D6371-05 explicitly states that the method is technically equivalent to EN 116, which was confirmed by the laboratory. Consequently, the two datasets should be equivalent, too, and agree within the limits given by the methods, which is not the case.

In the normal and correct operation of the test method EN 116, the difference between two single and independent results may exceed the values indicated by the formula *3.0-0.060X* (where X is the average of two results being compared) in not more than one case in twenty [10].

According to ASTM 6371-05, the difference between two single and independent results may exceed the values indicated by the formula *0.102(25-X)* (where X is the average of two results being compared) in not more than one case in twenty [12].

The 12 measurements from laboratory 7 ranged from -29 °C to -21 °C; for this pair of data (difference of 8 °C) the resulting reproducibility limits (4.5 °C for the EN method and 5.1 °C for the ASTM) are exceeded. Finally, all possible differences between the results of the two datasets were calculated. 66 combinations of results can be calculated, of which 11 differed by more than 6 °C and 16 by more than 5 °C, which exceeds the one in twenty criterion.

All other laboratories fulfilled the method performance criteria.

Thus the final number of datasets accepted for CFPP was 15 and for the CP 19.

The datasets accepted based on technical reasons were tested for normality of dataset means using kurtosis/skewness tests and normal probability plots and were tested for outlying means using the Grubbs test and using the Cochran test for outlying standard deviations, (both at a 99 % confidence level). Standard deviations within (s_{within}) and between ($s_{between}$) laboratories were calculated using one-way ANOVA. The results of these evaluations are shown in Table 4.

Table 4: Statistical evaluation of the technically accepted datasets for ERM-EF004.

p: number of technically valid datasets

Parameter	*p*	Outliers		Normally distributed	Statistical parameters			
		Means	Variances		Mean [°C]	*s* [°C]	$s_{between}$ [°C]	s_{within} [°C]
CFPP	15	none	none	yes	-27.92	2.06	1.99	1.16
CP	19	none	yes (L13 ISO 3015)	yes	-6.84	0.51	0.48	0.43

In all cases the laboratory means follow normal distributions. None of the data contains outlying means.

For the CP laboratory 13 (ISO method) was flagged as an outlier of variance at a 99 % confidence level. This is not an exclusion criterion itself. This demonstrates that the proficiency of this laboratory in applying the respective method is worse than the one of the other laboratories. The dataset was retained, as all results still agree with the reproducibility requirements of the respective documentary standards.

All datasets are considered consistent and the mean of laboratory means is a good estimate of the true value. Standard deviations between laboratories are considerably larger than the standard deviation within laboratories, showing that confidence intervals of replicate measurements are unsuitable as estimate of measurement uncertainty. The uncertainty related to the characterisation is estimated as the standard error of the mean of laboratory means (Table 5).

Table 5: Uncertainty of characterisation for ERM-EF004

Parameter	*p*	Mean [°C]	*s* [°C]	u_{char} [°C]
Cold filter plugging point	15	-27.92	2.06	0.53
Cloud point	19	-6.84	0.51	0.12

7 Value Assignment

Certified values are values that fulfil the highest standards of accuracy. Procedures at the JRC require generally pooling of not less than 6 datasets to assign certified values. Full uncertainty budgets in accordance with the 'Guide to the Expression of Uncertainty in Measurement' [4] were established.

7.1 Certified values and their uncertainties

The unweighted mean of the means of the accepted datasets as shown in Table 5 was assigned as certified value for each parameter.

The assigned uncertainty consists of uncertainties relating to characterisation, u_{char} (Section 6), potential between-unit inhomogeneity, u_{bb} (Section 4.1), and potential degradation during transport, u_{sts}, and long-term storage, u_{lts} (Section 5.3). These different contributions were combined to estimate the relative expanded uncertainty of the certified value (U_{CRM}) with a coverage factor k given as:

$$U_{CRM} = k \cdot \sqrt{u_{bb}^2 + u_{sts}^2 + u_{lts}^2 + u_{char}^2} \qquad \textbf{Equation 9}$$

- u_{char} was estimated as described in Section 6
- u_{bb} was estimated as described in Section 4.1.
- u_{sts} and u_{lts} were estimated as described in section 5.3

Because of the sufficient numbers of the degrees of freedom of the different uncertainty contributions, a coverage factor k of 2 was applied, to obtain the expanded uncertainties. The certified values and their uncertainties are summarised in Table 6.

Table 6: Certified values and their uncertainties for ERM-EF004

	Certified value [°C]	u_{char} [°C]	u_{bb} [°C]	u_{sts} [°C]	$u_{lts,}$ [°C]	U_{CRM} [1)] [°C]
CFPP	-27.9	0.53	0.58	0.14	1.04	2.7
CP	-6.8	0.117	0.081	0.055	0.088	0.4

[1)] Expanded (k = 2) and rounded uncertainty.

8 Metrological traceability and commutability

8.1 Metrological traceability

Identity

CFPP is a method-defined measurand and can only be obtained by following the procedure specified in EN 116:2015 [10] or ASTM D6371-05:2010 [12].

CP is a method-defined measurand and can only be obtained by following the procedure specified in ISO 3015:1992 [11] (equivalent to EN 23015:1994 [13]) or ASTM D2500-09:2011 [14].

Adherence to this procedure was confirmed by agreement of the laboratories' results with the assigned value for the CRM that was used as quality control sample. The measurand is therefore operationally defined by the methods as specified above.

Quantity value

Traceability of the obtained results is based on the traceability of all relevant input factors. Instruments in individual laboratories were verified and calibrated with tools ensuring traceability to the International System of units (SI). Additionally, the adequacy of the measures taken to ensure proper calibration of equipment and the traceability of results was verified by quality control samples being CRMs. All technically accepted datasets are therefore traceable to the same reference, namely the SI. This traceability to the same reference is also confirmed by the agreement of results within their respective uncertainties. As the assigned values are combinations of agreeing results individually traceable to the SI, the assigned quantity values themselves are traceable to the SI as well.

8.2 Commutability

Many measurement procedures include one or more steps which select specific (or specific groups of) analytes from the sample for the subsequent whole measurement process. Often the complete identity of these 'intermediate analytes' is not fully known or taken into account. Therefore, it is difficult to mimic all analytically relevant properties of real samples within a CRM. The degree of equivalence in the analytical behaviour of real samples and a CRM with respect to various measurement procedures (methods) is summarised in a concept called 'commutability of a reference material'. There are various definitions that define this concept. For instance, the CLSI Guideline C53-A [42] recommends the use of the following definition for the term *commutability*:

> "The equivalence of the mathematical relationships among the results of different measurement procedures for an RM and for representative samples of the type intended to be measured."

The commutability of a CRM defines its fitness for use and is therefore a crucial characteristic when applying different measurement methods. When the commutability of a CRM is not established, the results from routinely used methods cannot be legitimately compared with the certified value to determine whether a bias does not exist in calibration, nor can the CRM be used as a calibrant.

As the material comes from an industrial diesel producing plant having the same composition as a commercial automotive diesel, it is representative for other diesel samples and the analytical behaviour will be the same as for a routine diesel (B7) sample.

9 Instructions for use

9.1 Safety information

The classification is according to Regulation (EC) No. 1272/2008 [43] and the usual hazard and precautionary phrases for diesel apply:

H226 - Flammable liquid and vapour.
H304 - May be fatal if swallowed and enters airways.
H351 - Suspected of causing cancer.
H411 - Toxic to aquatic life with long lasting effects.

P210 - Keep away from heat/ /sparks/open flames/hot surfaces. No smoking.
P273 - Avoid release to the environment.
P280 - Wear protective gloves/protective clothing/eye protection/face protection.
P301+P310 - IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician.
P308+P313 - IF exposed or concerned: Get medical advice/attention.

9.2 Storage conditions

The materials should be stored at (18 ± 5) °C in the dark. Care should be taken once the units are open. The user should close any units immediately after taking a sample.

Please note that the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially for opened units.

9.3 Preparation and use of the material

The contents of the two ampoules shall be pooled to obtain one sample of 50 mL. No further sample treatment is necessary.

9.4 Minimum sample intake

The minimum sample intake is the required sample volume stipulated in the respective documentary standards, usually 50 mL.

9.5 Use of the certified value

The main purpose of these materials is to assess method performance, i.e. for checking accuracy of analytical results/calibration. As any reference material, it/they can be used for establishing control charts or validation studies.

Comparing an analytical result with the certified value

A result is unbiased if the combined standard uncertainty of measurement and certified value covers the difference between the certified value and the measurement result (see also ERM Application Note 1, https://crm.jrc.ec.europa.eu/ [39].

When assessing the method performance, the measured values of the CRMs are compared with the certified values. The procedure is summarised here:

- Calculate the absolute difference between mean measured value and the certified value (Δ_{meas}).

- Combine the measurement uncertainty (u_{meas}) with the uncertainty of the certified value (u_{CRM}): $u_{\Delta} = \sqrt{u_{meas}^2 + u_{CRM}^2}$
- Calculate the expanded uncertainty (U_{Δ}) from the combined uncertainty ($u_{\Delta,}$) using an appropriate coverage factor, corresponding to a level of confidence of approximately 95 %
- If $\Delta_{meas} \leq U_{\Delta}$ then no significant difference exists between the measurement result and the certified value, at a confidence level of approximately 95 %.

Use in quality control charts

The materials can be used for quality control charts. Using CRMs for quality control charts has the added value that a trueness assessment is built into the chart.

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Annexes

Annex A: Results of the homogeneity measurements

Annex B: Results of the short-term stability measurements

Annex C: Results of the long-term stability measurements

Annex D: Summary of methods used in the characterisation study

Annex E: Results of the characterisation measurements

Annex A: Results of the homogeneity measurements

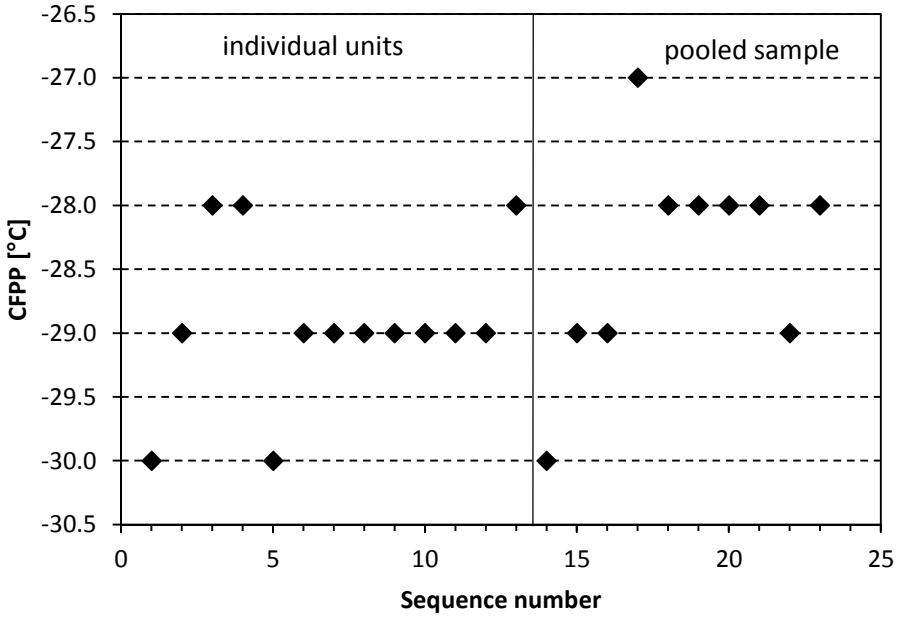

Figure A1: Individual measurements for CFPP in the order of measurement. (Sequence number: measurements on 13 individual units and 10 measurements from pooled sample)

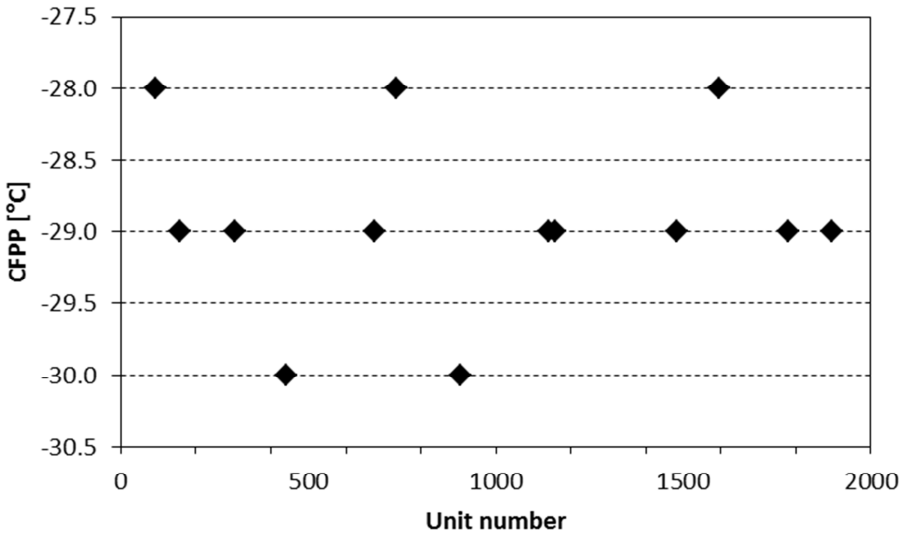

Figure A2: Unit values for CFPP against unit number.

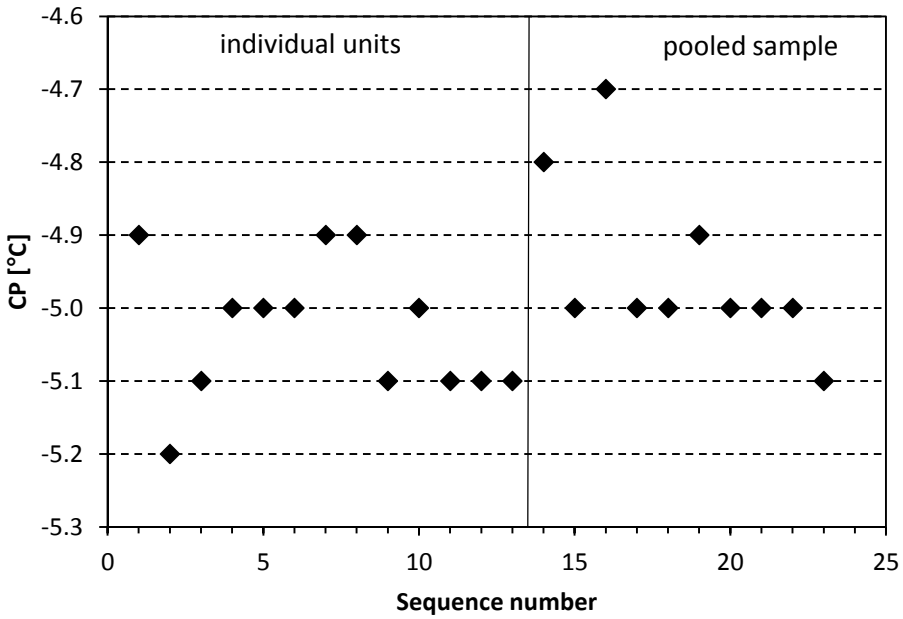

Figure A3: Individual measurements for CP in the order of measurement. (Sequence number: measurements on 13 individual units and 10 measurements from pooled sample)

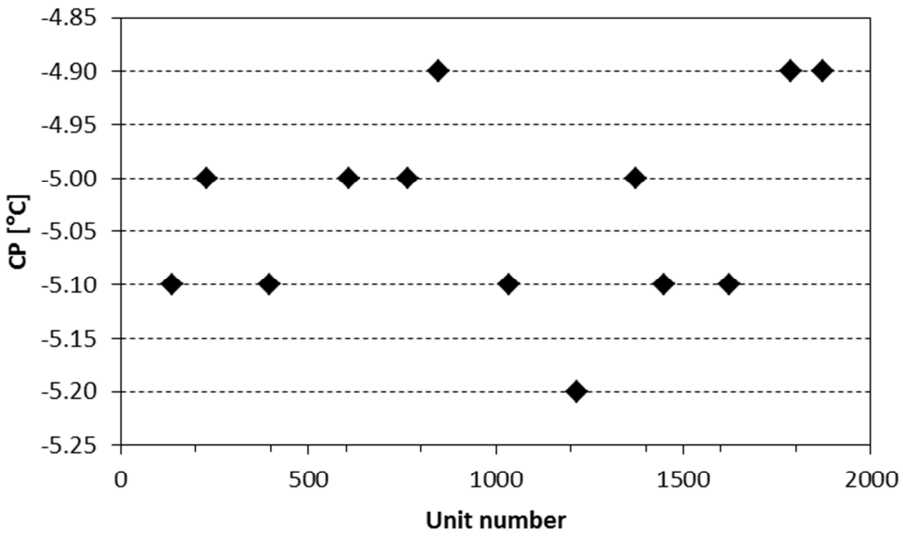

Figure A4: Unit values for CP against unit number.

Annex B: Results of the short-term stability measurements

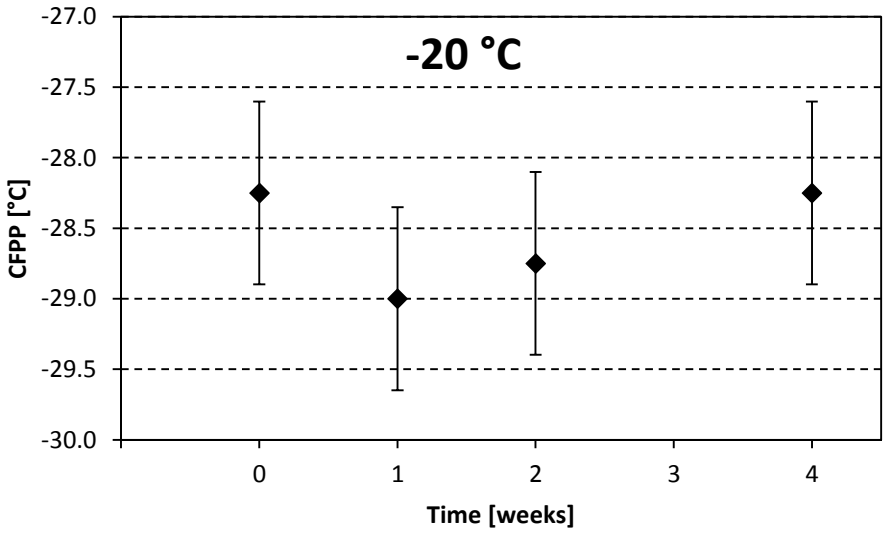

Figure B1: CFPP means measured at -20 °C at each time-point. Vertical bars represent the 95 % confidence interval of the mean, based on the within-group standard deviation as obtained by single-factor ANOVA.

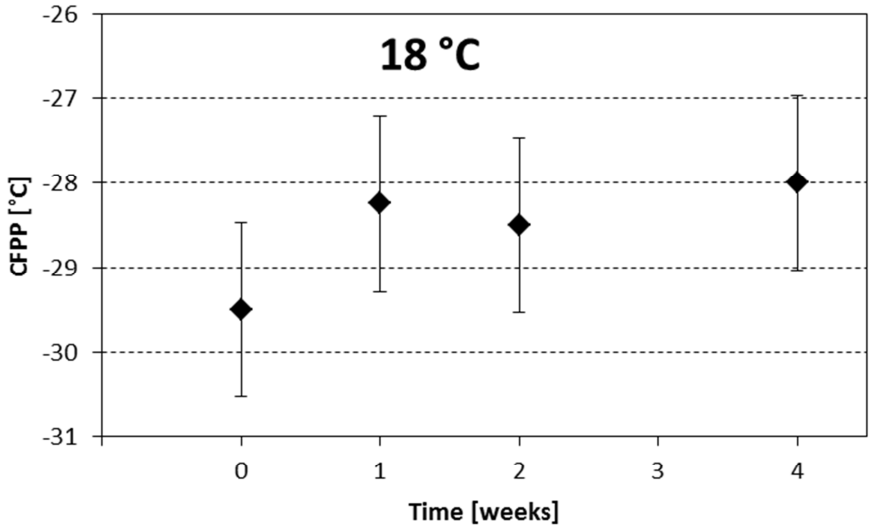

Figure B2: CFPP means measured at 18 °C at each time-point. Vertical bars represent the 95 % confidence interval of the mean, based on the within-group standard deviation as obtained by single-factor ANOVA.

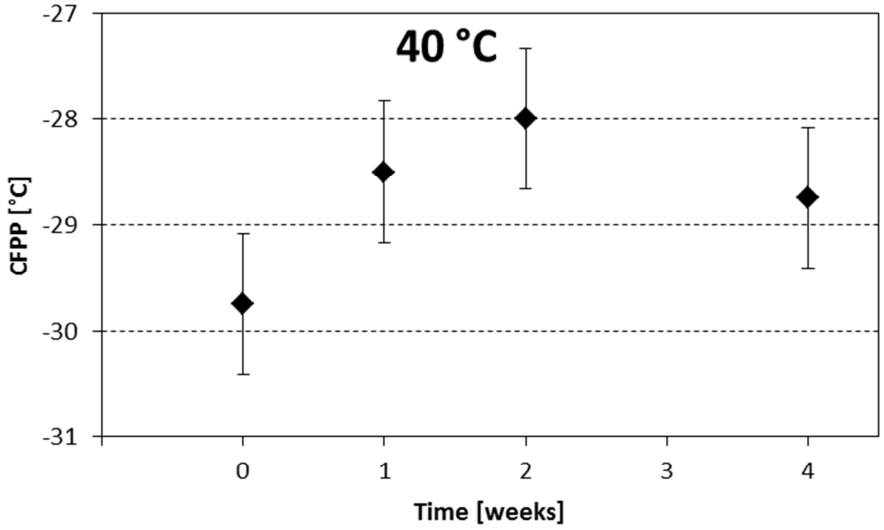

Figure B3: CFPP means measured at 40 °C each time-point. Vertical bars represent the 95 % confidence interval of the mean, based on the within-group standard deviation as obtained by single-factor ANOVA.

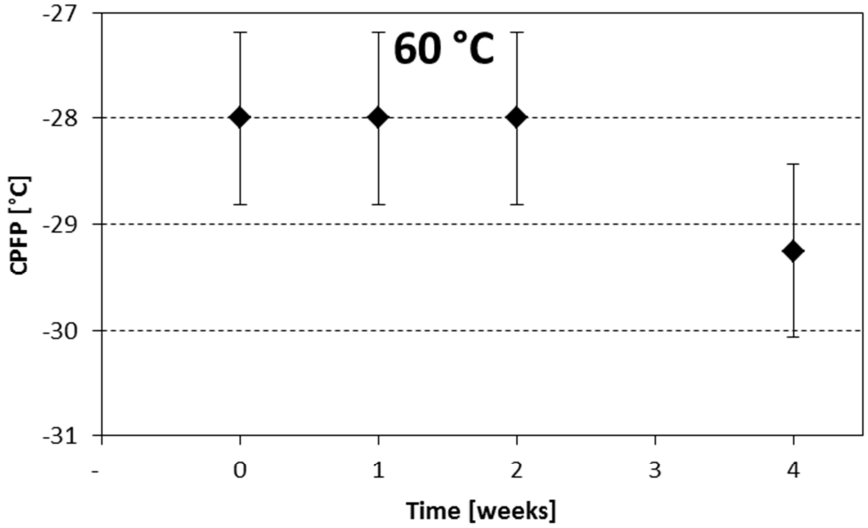

Figure B4: CFPP means measured at 60 °C each time-point. Vertical bars represent the 95 % confidence interval of the mean, based on the within-group standard deviation as obtained by single-factor ANOVA.

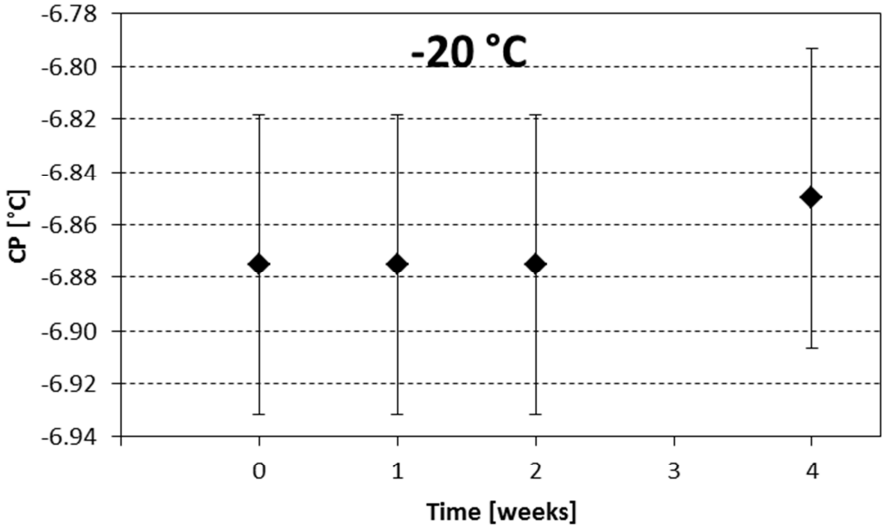

Figure B5: CP means measured at -20 °C at each time-point. Vertical bars represent the 95 % confidence interval of the mean, based on the within-group standard deviation as obtained by single-factor ANOVA.

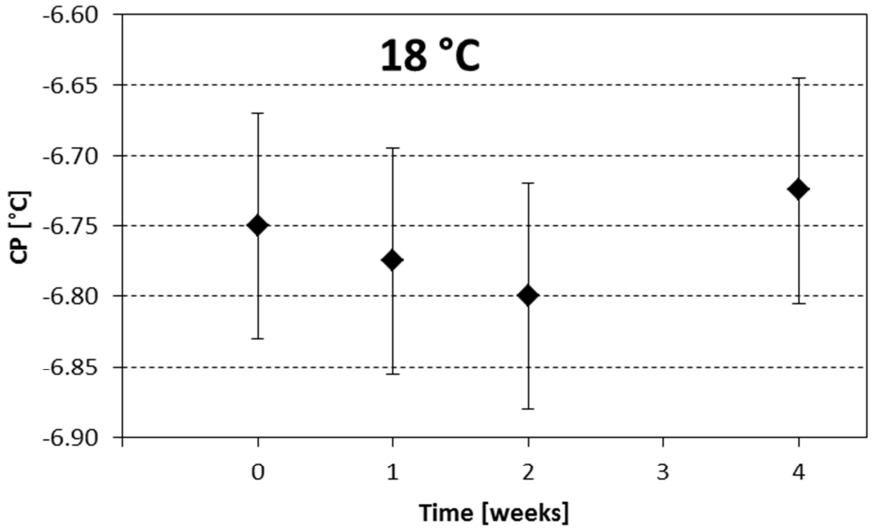

Figure B6: CP means measured at 18 °C at each time-point. Vertical bars represent the 95 % confidence interval of the mean, based on the within-group standard deviation as obtained by single-factor ANOVA.

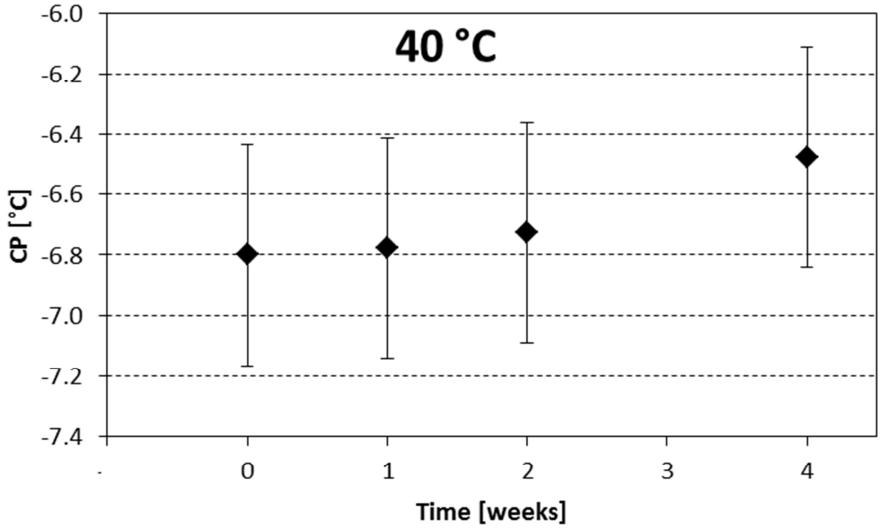

Figure B7: CP means measured at 40 °C at each time-point. Vertical bars represent the 95 % confidence interval of the mean, based on the within-group standard deviation as obtained by single-factor ANOVA.

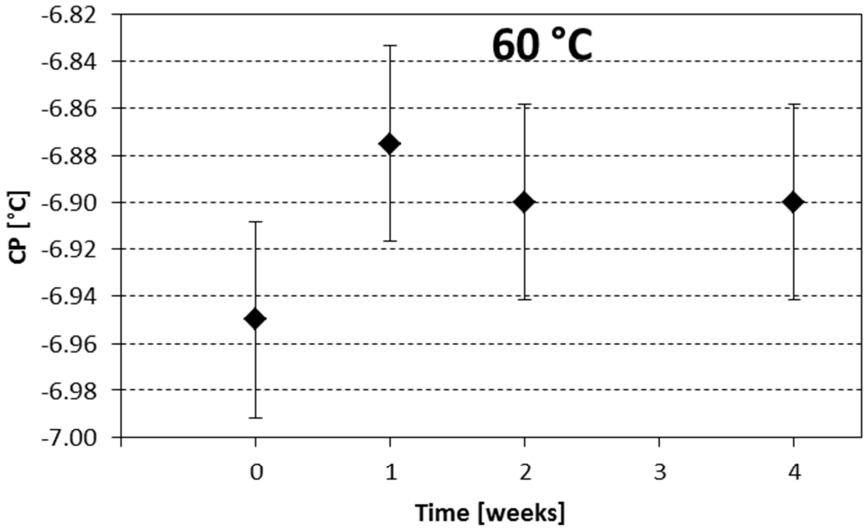

Figure B8: CP means measured at 60 °C at each time-point. Vertical bars represent the 95 % confidence interval of the mean, based on the within-group standard deviation as obtained by single-factor ANOVA.

Annex C: Results of the long-term stability measurements at 18 °C

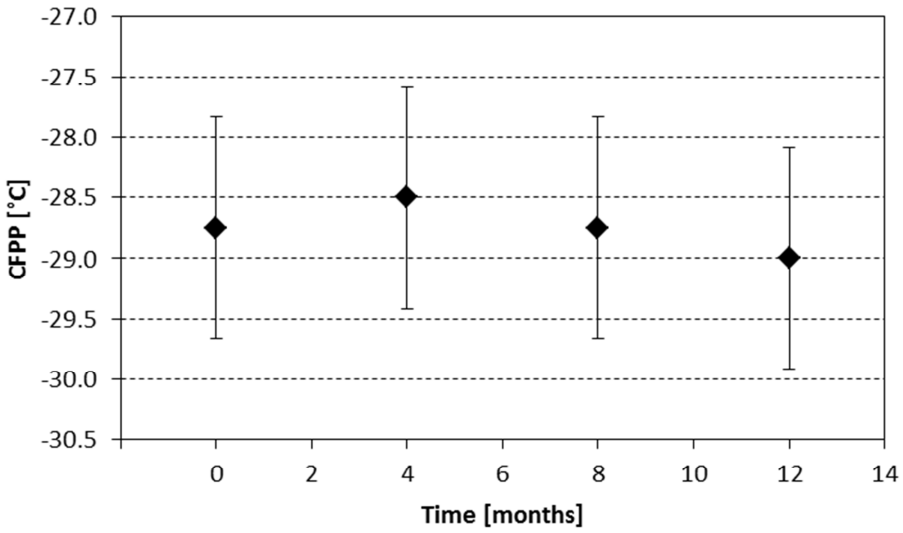

Figure C1: CFPP means measured at each time-point. Vertical bars represent the 95 % confidence interval of the mean, based on the within-group standard deviation as obtained by single-factor ANOVA.

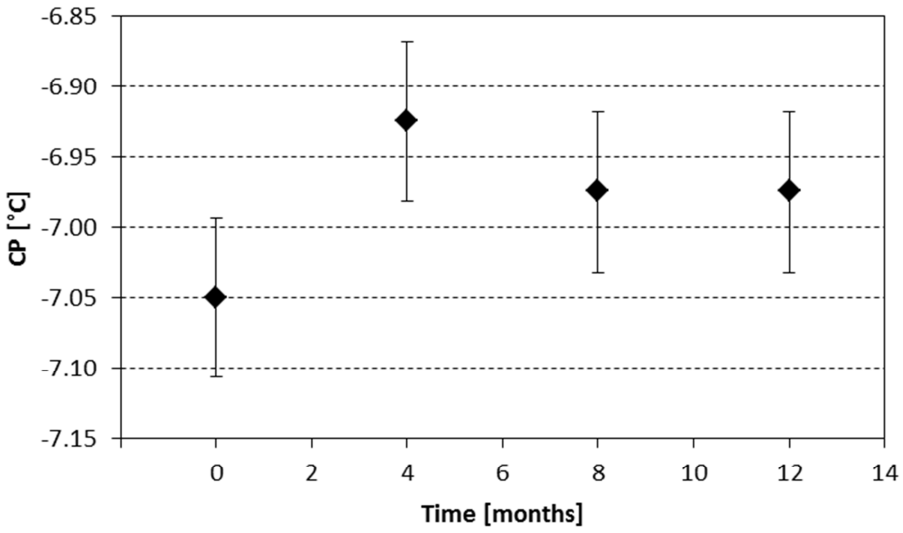

Figure C2: CP means measured at each time-point. Vertical bars represent the 95 % confidence interval of the mean, based on the within-group standard deviation as obtained by single-factor ANOVA.

Annex D: Summary of methods used in the characterisation study

Table D1. Overview on scope and principles of EN 116:2015 [10]

Standard Reference	**EN 116:2015**
Technical Body	CEN/TC 307 - Oilseeds, vegetable and animal fats and oils and their by-products - Methods of sampling and analysis
Title	Diesel and domestic heating fuels - Determination of **Cold Filter Plugging Point -** Stepwise cooling bath method
Scope	This European Standard specifies a method for the determination of the cold filter plugging point (CFPP) of diesel and domestic heating fuels (see 3.1) using automated test equipment. Manual test equipment may be used, but for referee purposes only automated test equipment is allowed. This European Standard is applicable to fatty-acid methyl esters (FAME) and to distillate fuels as well as paraffinic diesel fuels, including those containing FAME, flow-improvers or other additives, intended for use in diesel engines and domestic heating installations. The results obtained from the method specified in this European Standard are suitable for estimating the lowest temperature at which a fuel will give trouble-free flow in the fuel system. NOTE In the case of diesel fuels the results are usually close to the temperature of failure in service except when the fuel system contains, for example, a paper filter installed in a location exposed to the weather or if the filter plugging temperature is more than 12 °C below the cloud point of the fuel. Domestic heating installations are usually less critical and often operate satisfactorily at temperatures somewhat lower than those indicated by the test results. The difference in results obtained from the sample "as received" and after heat treatment at 45°C for 30 min may be used to investigate complaints of unsatisfactory performance under low temperature conditions. WARNING - The use of this standard may involve hazardous materials, operations and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.
Principle	A test portion of the fuel is cooled under the specified conditions and is drawn at intervals of 1 °C into a pipette under a controlled vacuum of 2 kPa through a standardized wire mesh filter. The procedure is repeated, as the fuel continues to cool, for each 1 °C below the first test temperature. Testing is continued until the amount of wax crystals which have separated out of solution is sufficient to stop or slow down the flow so that the time taken to fill the pipette exceeds 60 s or the fuel fails to return completely to the test jar before the fuel has cooled by a further 1 °C. The indicated temperature at which the last filtration was commenced is recorded as the cold filter plugging point (CFPP).

Table D2. Overview on scope and principles of ASTM D6371-05 [12]

Standard Reference	**ASTM D6371-05**
Technical Body	This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.07 on Flow Properties.
Title	Standard Test Method for **Cold Filter Plugging Point** of Diesel and Heating Fuels
Scope	This test method covers the determination of the cold filter plugging point (CFPP) temperature of diesel and domestic heating fuels using either manual or automated apparatus. NOTE 1—This test method is technically equivalent to test methods IP 309 and EN 116. The manual apparatus and automated apparatus are both suitable for referee purposes. This test method is applicable to distillate fuels, including those containing a flow-improving or other additive, intended for use in diesel engines and domestic heating installations. The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard. This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.
Principle	A specimen of the sample is cooled under specified conditions and, at intervals of 1 °C, is drawn into a pipet under a controlled vacuum through a standardized wire mesh filter. The procedure is repeated, as the specimen continues to cool, for each 1 °C below the first test temperature. Testing is continued until the amount of wax crystals that have separated out of solution is sufficient to stop or slow down the flow so that the time taken to fill the pipet exceeds 60 s or the fuel fails to return completely to the test jar before the fuel has cooled by a further 1 °C. The indicated temperature at which the last filtration was commenced is recorded as the CFPP.

Table D3. Overview on scope and principles of ISO 3015:1992 [11]

Standard Reference	**ISO 3015:1992 (EN 23015:1994)**
Technical Body	ISO/TC 28 Petroleum and related products, fuels and lubricants from natural or synthetic sources
Title	Petroleum products - Determination of **Cloud Point**
Scope	This International Standard specifies a method for the determination of the cloud point of petroleum products which are transparent in layers 40 mm in thickness and have a cloud point below 49 °C.
Principle	A sample is cooled at a specified rate and examined periodically. The temperature at which a cloud is first observed at the bottom of the test jar is recorded as the CP.

Table D4. Overview on scope and principles of ASTM D2500-09 [14]

Standard Reference	**ASTM D2500-09**
Technical Body	This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.07 on Flow Properties.
Title	Standard Test Method for **Cloud Point** of Petroleum Products
Scope	This test method covers only petroleum products and biodiesel fuels that are transparent in layers 40 mm in thickness, and with a cloud point below 49°C. NOTE 1—The interlaboratory program consisted of petroleum products of Test Method D 1500 color of 3.5 and lower. The precisions stated in this test method may not apply to samples with ASTM color higher than 3.5. The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard. This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.
Principle	The specimen is cooled at a specified rate and examined periodically. The temperature at which a cloud is first observed at the bottom of the test jar is recorded as the cloud point.

Table D5: Precision data as laid down in respective documentary standards and estimated expanded measurement uncertainties for 6 replicates

Parameter	Unit	r	R	U_{meas}
CFPP EN116:2015 [10]	[°C]	1.2-(0.027 x C[1)])	3.0-(0.06 x C)	3.09
CFPP ASTM D6371-05:2010 [12]	[°C]	1.76	0.102 x (25 - C)	3.56
CP ISO 3015:1992 [11]	[°C]	2	4	2.54
CP ASTM D2500-09:2011 [14]	[°C]	2	4	2.54

[1)] C=Determined result

Annex E: Results of the characterisation measurements

Note: For the measurement uncertainties of the individual laboratories the measurement uncertainties derived from the standard methods were taken.

Table E1: CFPP in diesel (B7) as reported by each individual lab

Laboratory code	replicate 1 [°C]	replicate 2 [°C]	replicate 3 [°C]	replicate 4 [°C]	replicate 5 [°C]	replicate 6 [°C]	mean [°C]	SD [°C]
L1 EN 116	-28	-27	-28	-29	-29	-29	-28.3	0.82
L2 EN 116	-28	-28	-31	-29	-32	-29	-29.5	1.64
L2 ASTM D6371	-30	-29	-29	-31	0	-29	-29.6	0.89
L3 EN 116	-27	-28	-27	-25	-26	-28	-26.8	1.17
L5 EN 116	-29	-27	-28	-28	-27	-27	-27.7	0.82
L6 EN 116	-30	-30	-30	-27	-29	-28	-29.0	1.26
L8 EN 116	-26	-24	-24	-23	-24	-23	-24.0	1.10
L8 ASTM D6371	-24	-24	-25	-23	-25	-24	-24.2	0.75
L9 EN 116	-29	-30	-28	-29	-30	-30	-29.3	0.82
L10 EN 116	-25	-27	-27	-27	-27	-27	-26.7	0.82
L11 EN 116	-28	-32	-29	-32		-32	-30.6	1.95
L12 EN 116	-30	-30	-28	-29	-28	-29	-29.0	0.89
L13 EN 116	-28	-31	-29	-28	-31	-29	-29.3	1.37
L13 ASTM D6371	-29	-30	-30	-26	-31	-30	-29.3	1.75
L14 EN 116	-26	-25	-26	-25	-25	-26	-25.5	0.55
Results not used for certification								
L3 ASTM D6371	*-23.0*	*-28.0*	*-28.0*	*-27.0*	*-23.0*	*-29.0*	*-26.3*	*2.66*
L7 EN 116	*-27.0*	*-25.0*	*-25.0*	*-28.0*	*-29.0*	*-26.0*	*-26.7*	*1.63*
L7 ASTM D6371	*-22.0*	*-22.0*	*-24.0*	*-22.0*	*-22.0*	*-21.0*	*-22.2*	*0.98*

* laboratory could not report a value as they did not have enough sample to do the measurement

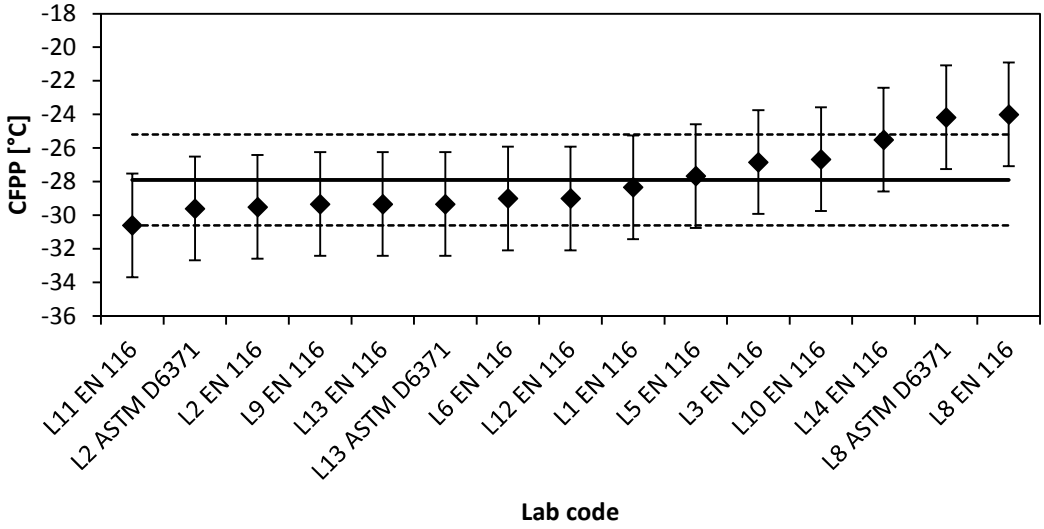

Figure E1: Results of the characterisation study for the CFPP in diesel (B7) measured using EN 116:2015 [10] and ASTM D6371-05:2010 [12] (continuous line: certified value; dashed line: expanded uncertainty with k=2; error bars: expanded measurement uncertainty as given in Table D5)

Table E2: CP in diesel (B7) as reported by each individual lab

Laboratory code	replicate 1 [°C]	replicate 2 [°C]	replicate 3 [°C]	replicate 4 [°C]	replicate 5 [°C]	replicate 6 [°C]	mean [°C]	SD [°C]
L1 ISO 3015	-7	-7	-7	-7	-7	-7	-7.0	0.00
L2 ISO 3015	-7	-7	-7	-7	-7	-7	-7.0	0.00
L2 ASTM D2500	-7	-7	-7	-7	-7	-7	-6.7	0.09
L3 ISO 3015	-6	-7	-7	-7	-7	-7	-6.8	0.41
L3 ASTM D2500	-7	-7	-7	-7	-8	-8	-7.3	0.52
L5 ISO 3015	-6	-7	-7	-7	-7	-7	-6.8	0.41
L5 ASTM D2500	-6	-7	-7	-7	-7	-7	-6.8	0.41
L6 ISO 3015	-7	-7	-7	-7	-7	-7	-6.9	0.04
L7 ISO 3015	-6	-7	-6	-7	-7	-6	-6.5	0.55
L7 ASTM D2500	-6	-6	-7	-7	-6	-6	-6.3	0.52
L8 ISO 3015	-7	-6	-6	-7	-6	-7	-6.5	0.55
L8 ASTM D2500	-7	-6	-6	-7	-7	-7	-6.7	0.52
L9 ISO 3015	-7	-7	-7	-7	-7	-7	-7.0	0.00
L11 ISO 3015	-8	-8	-8	-8	-8	-8	-8.0	0.00
L11 ASTM D2500	-8	-8	-8	-8	-8	-8	-8.0	0.00
L12 ISO 3015	-7	-7	-7	-7	-7	-7	-7.0	0.15
L13 ISO 3015	-5	-7	-6	-5	-8	-6	-6.2	1.07
L13 ASTM D2500	-5	-7	-6	-6	-7	-6	-6.3	0.69
L14 ISO 3015	-6	-6	-6	-6	-6	-6	-6.2	0.11

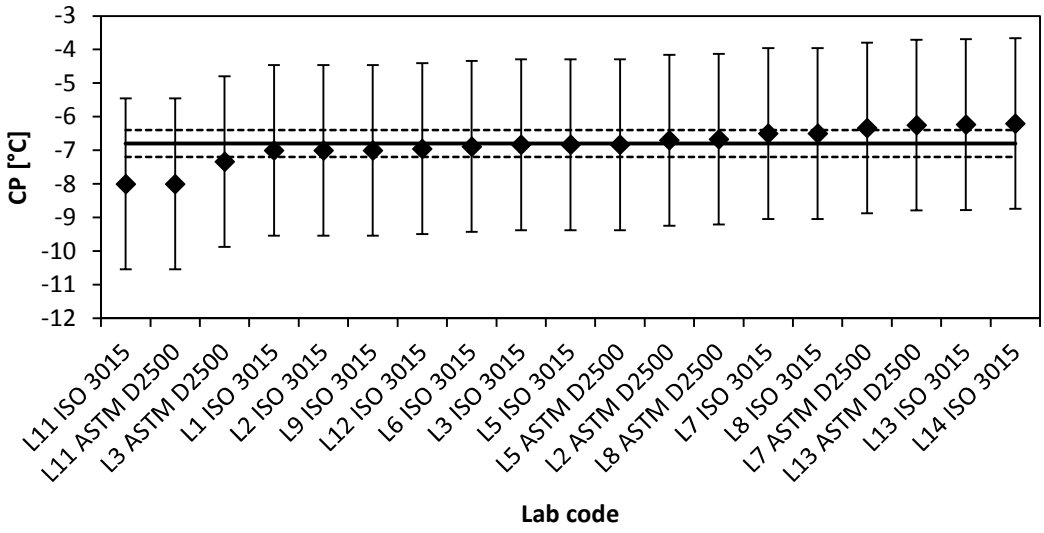

Figure E2: Results of the characterisation study for the CP in diesel (B7) measured using ISO 3015:1992 [11] and ASTM D2500-09:2011 [14] (continuous line: certified value; dashed line: expanded uncertainty with k=2; error bars: expanded measurement uncertainty as given in Table D5)

European Commission

EUR 28893 EN – Joint Research Centre – Directorate F – Health, Consumers and Reference Materials

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Author(s): M. Ulberth-Buchgraber, J. Charoud-Got, H. Emteborg, A. Held
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