CERTIFICATION REPORT

Certification of the cold filter plugging point (CFPP) and the cloud point (CP) of gas oil

Certified Reference Material ERM®-FC395k

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Certification of the cold filter plugging point (CFPP) and the cloud point (CP) of gas oil

Certified Reference Material ERM®-FC395k

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Summary

This report describes the production of ERM-FC395k, a gas oil material certified for cold filter plugging point (CFPP) and cloud point (CP).

The material has been produced following ISO Guide 34:2009 [1].

A mixture of hydrotreated straight-run distillates and cracked diesel fractions without flow improvers and fatty acid methyl esters was obtained. The material was ampouled in amber glass ampoules.

Between unit-heterogeneity has been quantified and stability during dispatch and storage has been assessed in accordance with ISO Guide 35:2006 [2]. Within-unit heterogeneity has been quantified to determine the minimum sample intake.

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

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

The material is intended for the quality control and assessment of method performance. As any reference material, it can also be used for control charts or validation studies. The certified reference material (CRM) is available in sets of two glass ampoules containing each 27 mL of diesel closed under argon atmosphere. The contents of the two ampoules shall be mixed to obtain one sample of 50 mL.

The CRM has been accepted as European Reference Material (ERM®) after peer evaluation by the partners of the European Reference Materials consortium.

The following values were assigned:

	Certified value [3] [°C]	Uncertainty [4] [°C]
Cold filter plugging point (CFPP) [1]	-7.9	1.6
Cloud point (CP) [2]	-7.3	3.0

1) As defined by EN 116 or ASTM D6371 using the automatic or manual procedure.

2) As defined by EN 23015, ISO 3015 or ASTM D2500 using the automatic or manual procedure.

3) Unweighted mean value of the means of accepted sets of data, each set being obtained in a different laboratory and/or with a different method of determination. The certified value and its uncertainty are traceable to the International System of units (SI).

4) The certified uncertainty 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.

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.

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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 $y = a + bx$
BCR®	One of the trademarks of CRMs owned by the European Commission; formerly Community Bureau of Reference
CFPP	Cold filter plugging point
CP	Cloud point
CI	Confidence interval
CRM	Certified reference material
EC	European Commission
EN	European norm (standard)
ERM®	Trademark of European Reference Materials
EU	European Union
GUM	Guide to the Expression of Uncertainty in Measurements *[ISO/IEC Guide 98-3:2008]*
IRMM	Institute for Reference Materials and Measurements of the JRC
ISO	International Organization for Standardization
JRC	Joint Research Centre of the European Commission
k	Coverage factor
$MS_{between}$	Mean of squares between-unit from an ANOVA
MS_{within}	Mean of squares within-unit from an ANOVA
PTFE	Poly(tetrafluoroethylene)
QC	Quality control
RM	Reference material
RM Unit	Reference Materials Unit of the IRMM
RSD	Relative standard deviation
s	Standard deviation
s_{bb}	Between-unit standard deviation; an additional index "rel" is added as appropriate
$s_{between}$	Standard deviation between groups as obtained from ANOVA
SI	International System of Units
s_L	Standard deviation between laboratories
s_{meas}	Standard deviation of the results of the pooled samples from the homogeneity study
s_{meas}	Standard deviation of measurement data

s_r	Repeatability standard deviation; an additional index "rel" is added as appropriate
s_R	Reproducibility standard deviation; an additional index "rel" is added as appropriate
s_{wb}	Within-unit standard deviation
s_{within}	Standard deviation within groups as obtained from ANOVA
t	Time
T	Temperature
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
u	Standard uncertainty
U	Expanded uncertainty
u_{bb}	Standard uncertainty related to a possible between-unit heterogeneity; an additional index "rel" is added as appropriate
u_c	Combined standard uncertainty; an additional index "rel" is added as appropriate
$u_{c,bb}$	Standard deviation of the results of the 12 individual samples in the homogeneity study
u_{cal}	Standard uncertainty of calibration
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_m	Standard measurement uncertainty
U_{meas}	Expanded measurement uncertainty
u_{sts}	Standard uncertainty of the short-term stability
UWL	Upper warning limit
$\overline{x}$	Arithmetic mean
$\overline{x_{ns}}$	Arithmetic mean of all results of normal stock samples
$\overline{x_{ref}}$	Arithmetic mean of results of reference samples
α	Significance level

1 Introduction

1.1 Background: need for the CRM

Directive 98/70/EC of the European Parliament and of the Council of 13 October 1998 relating to the quality of petrol and diesel fuels sets quality criteria for petrol and diesel. Adherence to these criteria is vital for intra-EU trade and ensures – via the free movement of goods – the working of an efficient market in these products. One of the specifications that diesel fuels must meet is the cold filter plugging point (CFPP). Related to this is the cloud point (CP).

> **CFPP** is the lowest temperature at which a given volume of diesel still can pass through a filter. This gives an estimate down to which temperature diesel can be used without problems.
>
> **CP** is the temperature at which wax in diesel begins to precipitate, thus causing lower transmittance of light.

Both CFPP and CP are caused by the precipitation of paraffines at low temperatures. Naturally, a certain diesel (also called "gas oil") will first develop some precipitates, which reduce transmittance of light. Upon further cooling, the precipitates will be numerous and large enough to block the filter. Therefore, the CP is always higher than the CFPP.

Blocking of a filter depends on a multitude of parameters, such as the pore size of the filter, amount of volume to be filtered, pressure applied to push the liquid through the filter etc. Similarly, the formation of precipitates depends – amongst other factors - on the cooling rate. Therefore, neither CP nor CFPP are absolute values, but strongly depend on the conditions applied, i.e. they are method-defined properties. Standardisation is the method of choice to make results of such measurements comparable after all and a number of standards have been developed for the measurement of CFPP and CP. The main standards used for CFPP are EN116 [5] and ASTM D6371 [6] and ISO 3015 [7] (which is the same as EN 23015 [8]) and ASTM D2500 [9] for CP. Each of these methods describes a "manual method", i.e. a method where one sample after the other is filtered, but also gives specifications for "automated methods", which require minimal interaction by the operator. Both manual as well as automated methods are used nowadays. A closer look at the methods for CFPP and CP reveals that they differ only slightly in some specifications of thermometers, but that the specifications for the main steps are the same. The methods should therefore be equivalent. ASTM D6371 explicitly states that the method is technically equivalent to EN 116.

While standard methods go a long way to support comparability of results, they cannot guarantee that each laboratory applies the standard correctly. Certified reference materials (CRMs) are needed to give laboratories the possibility to demonstrate their method proficiency and proper working of their instruments. For this reason, the European Commission funded a project for the development of BCR-395 [10], a CRM for CFPP in 1990. As this material was sold out, the Institute for Reference Materials and Measurements (IRMM), one of the institutes of the European Commission's Joint Research Centre, decided to prepare a replacement of the material.

1.2 Analytical accuracy of the methods

ASTM D6371-05 and ASTM D2500-09 give information on expected repeatability and reproducibility standard deviations. The standards state that the difference between two measurements under repeatability conditions will not exceed 1.76 °C (CFPP) and 2 °C (CP) in one case out of 20 and that the difference between two measurements performed by different laboratories will not exceed 0.102*(25-x) °C (CFPP; x being the measured temperature) and 4 °C (CP) in one case out of 20. These limits are equivalent to warning

limits in a range control chart. Using the relevant equations one can derive the following relationship:

$$s_r = \frac{UWL}{d_2 + 2d_3} \qquad \text{Eq. (1)}$$

with UWL the upper warning limit and d_2 and d_3 constants found in the statistical literature [11] which solely depend on the size of the sample. For 2 observations, d_2 is 1.128 and d_3 is 0.853.

Using these equations, repeatability standard deviations (s_r) of 0.62 °C (CFPP) and 0.71 °C (CP) and reproducibility standard deviations (s_R) of 1.18 °C (CFPP at -7.7 °C) and 1.41 °C (CP) are obtained.

As the standard deviation between laboratories (s_L) is

$$s_L = \sqrt{s_R^2 - s_r^2} \qquad \text{Eq. (2)}$$

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

$$U_{meas} = 2 = \sqrt{s_L^2 - \frac{s_r^2}{n}} \qquad \text{Eq. (3)}$$

expanded uncertainties of 2.4 °C (CFPP at -7.7 °C) and 2.9 °C (CP) can be estimated for n=6 replicates.

1.3 Choice of the material

The goal of this project was to mimic as close as possible BCR-395, as this allows using experience gained from the stability of the previous material. Therefore, again a diesel without flow improving additives was chosen. In addition, care was taken to ensure that the diesel did not contain any biodiesel (fatty acid methyl esters).

As all diesels currently sold are mixtures of straight-run distillates and cracked components, also such a blend was selected.

1.4 Design of the project

Both CFPP and CP are method defined properties, which makes it very difficult to demonstrate absence of bias in a single laboratory. Certification by intercomparison was therefore chosen as certification approach.

In order to make the material as widely applicable as possible, care was taken to include automated as well as manual methods. In addition, laboratories claiming to adhere to the various equivalent standard methods were selected. The assigned values are therefore applicable to a wide range of standard methods and equipment.

2 Participants

2.1 Project management and evaluation

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No 268-TEST)

2.2 Processing

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No 268-TEST)

2.3 Homogeneity study

ITS Testing Services (UK) Ltd (West Thurrock Laboratory), West Thurrock, UK
(measurements under the scope of ISO/IEC 17025 accreditation UKAS No 0102)

2.4 Stability study

Eesti Keskkonnauuringute Keskus OÜ, Tallinn, EE
(measurements under the scope of ISO/IEC 17025 accreditation EAK L008)

Hansa group AG, Duisburg, DE
(measurements under the scope of ISO/IEC 17025 accreditation DAC-PL-0607-09)

2.5 Characterisation

Participants are listed in alphabetical order.

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

Asociación “BTC” para la investigación de combustibles convencionales y renovables, y medio ambiente, Bilbao, ES
(measurements under the scope of ISO/IEC 17025 accreditation ENAC No 40/LE901)

Eesti Keskkonnauuringute Keskus OÜ, Tallinn, EE
(measurements under the scope of ISO/IEC 17025 accreditation EAK L008)

Fundacion Cetena (Laboratorio Área de Materiales Poliméricos), Noain, Navarra, ES
(measurements under the scope of ISO/IEC 17025 accreditation ENAC No 69/LE1062)

Intertek OCA France, Donges, FR
(measurements under the scope of ISO/IEC 17025 accreditation Cofrac No 1-2158)

Intertek (Schweiz) AG, Schlieren, CH
(measurements under the scope of ISO/IEC 17025 accreditation STS No 452)

ITS Testing Services (UK) Ltd (West Thurrock Laboratory), West Thurrock, UK
(measurements under the scope of ISO/IEC 17025 accreditation UKAS No 0102)

ITS Testing Services (UK) Ltd (Teesside Laboratory), Cleveland, UK
(measurements under the scope of ISO/IEC 17025 accreditation UKAS No 4106)

Laboratorio de combustibles, Ferrol, ES
(measurements under the scope of ISO/IEC 17025 accreditation ENAC No 814/LE1688)

Oilcheck Pty Ltd, Sefton, AU
(measurements under the scope of ISO/IEC 17025 accreditation NATA 2031)

Southwest Research Institute, San Antonio, Texas, US
(measurements under the scope of ISO/IEC 17025 accreditation A2LA No 0702.04)

Stazione Sperimentale per Combustibili, San Donato Milanese, IT
(measurements under the scope of ISO/IEC 17025 accreditation ACCREDIA No 0173-1)

Vúrup, a.s., Bratislava, SK
(measurements under the scope of ISO/IEC 17025 accreditation SNAS No 049/S-119)

3 Material processing and process control

3.1 Origin of the starting material

The gas oil material (automotive diesel oil) was provided by Esso Belgium, division of ExxonMobil Petroleum & Chemical B.V.B.A., Antwerp (BE) and was produced by Esso Netherland B.V., Raffinaderij Rotterdam, Rotterdam-Botlek (NL). Diesel was taken directly from the refinery blender unit. The sampling spot was upstream, i.e. before the injection of additives, thus providing a mixture of straight-run distillates and cracked fractions without cold flow improving additives and fatty acid methyl esters. All blend streams are normal to severely hydro-processed, which improves the stability of the material.

Measurements at the refinery gave a CFPP of about -7 °C and a CP of about -6.6 °C. Eight 10 L jars diesel were delivered to IRMM, accompanied by a safety data sheet.

3.2 Processing

The contents of the cans were combined in one 100 L plastic drum and filtered through a paper filter to remove residual dust or metal particles. The material was stirred using a polytetrafluoroethylene (PTFE) paddle while the drum itself was flushed with argon. 30 mL amber glass ampoules were filled with 27 mL of diesel. The filling was stopped when the level of diesel was too low to be stirred by the PTFE paddle. In total, 2500 ampoules were filled.

3.3 Packaging

Each unit of reference material consists of a set of two amber glass ampoules, each containing 27 mL of gas oil. The content of the two ampoules must be mixed together before performing the measurement. In this report, the term "unit" refers to such a set of two ampoules that are mixed for analysis.

4 Assessment of homogeneity

A key requirement for any reference material (RM) is the equivalence between the various units. In this respect, it is not relevant whether the variation between units is significant compared to the analytical variation, but whether this variation is significant to the certified uncertainty. Consequently, ISO Guide 34 requires RM producers to quantify the between unit variation. This aspect is covered in between-unit homogeneity studies.

Within-unit heterogeneity is in this case not relevant, as the two ampoules need to be pooled to allow one single measurement.

The homogeneity assessment was done using EN 116 method (automated equipment) for the CFPP and using ISO 3015 method (automated equipment) for the CP.

4.1 Between-unit homogeneity

The between-unit homogeneity was evaluated to ensure that the certified values of the CRM are valid for all sets of the material, within the stated uncertainty.

The two ampoules of each set need to be pooled to allow one measurement. As different ampoules can be measured only once, the variability between results contains both repeatability and real between-unit variation. To avoid this problem and to obtain an assessment of the repeatability standard deviation of the laboratory, it was decided to pool several sets of ampoules, mix them and perform replicate measurements. The principle of the setup is shown in Figure 1.

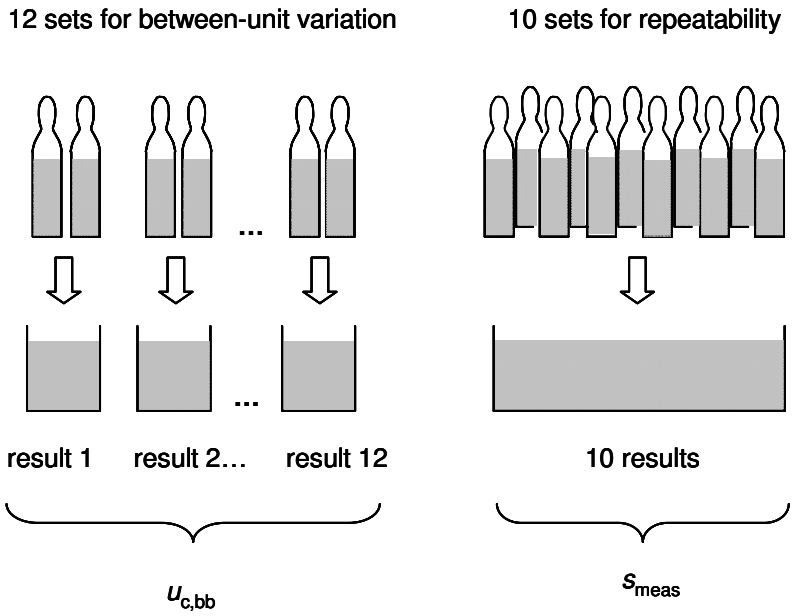

Figure 1: Setup of the between-unit homogeneity study

For each method 22 sets were selected using a random stratified sampling scheme covering the whole batch. Of the 22 sets, 12 were measured once after pooling the content of the two ampoules belonging to one set. The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend in the filling sequence. The other 10 sets were pooled together and the mixture was divided in 10 aliquots, each measured once under repeatability conditions. The results are shown as graphs in Annex A.

Regression analyses were performed to evaluate potential trends in the filling sequence. No trends in the filling sequence were visible (not significant on a 95 % confidence level). Both EN116 and ISO 3015 give results rounded to full digits. Therefore, outlier testing is not suitable for testing the data for consistency, but a test was made whether the results fulfil the repeatability criteria set in the standards. For this, all possible differences between results under repeatability conditions were calculated. The data for CFPP ranged from -7 to -9 °C; 66 combinations of results can be made, of which only 4 differed by more than 1.76 °C, which is slightly higher than the 5 % stated in the standard. For CP, results ranged from -5 to -8 °C, with 3 combinations differing by more than 2 °C, which is also slightly higher than the 5 % stated in the standard. As the deviations from the standard were small, the data were accepted as consistent with the standards.

To obtain the standard deviation between units (s_{bb}), the standard deviation from the 10 individual units ($u_{c,bb}$) must be corrected for the pure measurement standard deviation (s_{meas}) as shown in equation (4) [12].

$$s_{bb} = \sqrt{u_{c,bb}^2 - s_{meas}^2} \qquad \text{Eq. (4)}$$

As the methods give results in °C without digits, Monte-Carlo simulations were performed to obtain standard deviations. For each individual result, 1000 random numbers were generated using Statistica 7 (StatSoft Inc, Tulsa, US). The random numbers for each individual result follow a rectangular distribution of ± 0.5 °C around the measured value. For each of the resulting 1000 datasets, the standard deviations between individual units ($u_{c,bb}$), the pooled units (s_{meas}) and s_{bb} were calculated. For CP, 5 values for s_{bb} had to be deleted, as $u_{c,bb}$ was

smaller than s_{meas}. This can occur by random fluctuations and removal of these s_{bb} values creates an insignificantly small bias towards higher values for s_{bb}. The average of the 1000 s_{bb} values was adopted as best estimate of s_{bb}. The results of these calculations are summarised in Table 1.

Table 1: Results of the statistical evaluation

	Average $u_{c,bb}$ [°C]	average s_{meas} [°C]	s_{bb} [°C]
CFPP	0.68	0.28	0.61
CP	0.90	0.60	0.66

s_{bb} was adopted as uncertainty contribution to account for potential heterogeneity.

4.2 Within-unit homogeneity and minimum sample intake

The minimum sample intake is defined by the standard methods. In both cases, the contents of two ampoules must be pooled to a single analysis sample.

5 Stability

Stability testing of the reference material is necessary to establish conditions for storage (long-term stability) as well as conditions for dispatch to the customers (short-term stability). During transport, especially in summer time, temperatures up to 60 °C might be reached and stability against these conditions must be demonstrated if transport at ambient temperature will be applied.

The use of diesel in shipping, aviation, road transport and driving other engines often requires storage in hot and humid climates. A significant number of studies have been performed to determine storage and temperature stability of diesels. The sections below summarises the findings reviewed by Batts and Zuhdan Fathoni [13] and Pedley and coworkers [14]. The main focus of stability studies on diesel oil is the creation of sediments ("gum"), which leads to a lower filterability and eventually blocking of filters. This gumming is primarily an effect of acid-base reactions, oxidadive gum reactions and esterifications. Several factors have been identified to affect the amount of gum formation:

- Straight-run distillates show markedly lower gum formation than diesel containing significant amounts of cracked distillates. This effect is explained by the higher number of double bounds and aromatics in cracked distillates, which have been shown to be less stable than paraffines.
- Heteroatoms, especially N and S, increase the rate of gum formation and the resulting sediments are enriched in N and S. The negative effect depends on the compound; thiphene and aromatic thiols were found to be more harmful than aliphatic thiols and non-basic N-compounds being more harmful than basic ones.
- Oxygen contact greatly decreases stability. This also applies to dissolved oxygen: deoxygenated diesel was found to produce only 1/5 of the amount of sediment than aerated one.
- Light, either as sun or ultraviolet radiation, is a strong catalyst for sediment formation, with samples stored under sunlight or ultraviolet radiation producing sediment 10 times faster than samples stored in the dark. However, exclusion of light alone does also not prevent sediment formation.
- The container material can have an influence, with metals catalysing degradation. In some studies soft glass was found to have a stabilising effect, whereas in other

studies using relatively stable diesels, no advantage of soft glass over borosilicate glass was found.

- Elevated pressure also reduces stability of diesels.

Experiments show that gumming reactions in the dark are following the Arrhenius law with a doubling of the reaction rate for every 10 °C increase of temperature. Sunlight and UV radiation lead to initially faster gumming rates. This temperature dependence also led to the development of a number of accelerated degradation studies. Bottles stored for 13 weeks at + 43 °C were found to show the same degradation behaviour than bottles stored at 18-24 °C for 1 year. Another study found that 4 weeks storage at +120 °F (49 °C) gave satisfactory correlation for predicting the amount of sediment for 12-18 months storage.

These data show that time, temperature and radiation are regarded as the most relevant influences on stability of diesel materials. The influence of ultraviolet or visible radiation was minimised by the choice of the containment which eliminates most of the incoming light. In addition, materials are stored and dispatched in the dark, thus practically eliminating the possibility of radiative degradation. The ampoules are closed, thus preventing additional contact with oxygen. Therefore, only the influences of time and temperature needed to be investigated.

The stability studies have been carried out using an isochronous design [15]. In that approach, samples are stored for a certain time at different temperature conditions. Afterwards, the samples are moved to conditions where further degradation can be assumed to be negligible ("reference conditions"), effectively "freezing" the degradation status of the materials. At the end of the isochronous storage, the samples are analysed simultaneously under repeatability conditions. Analysis of the material (after various exposure times and temperatures) under repeatability conditions greatly improves the sensitivity of the stability tests. The assessment of stability (short-term and long-term) was done using EN 116 method (automated equipment) for the CFPP and ISO 3015 method (automated equipment) for the CP.

Additional information on the long-term stability was available from the previous material BCR-395: stability monitoring organised by IRMM had shown no change in the values over 16 years. Therefore, stability studies were organised mainly to confirm that the new material behaves similar to the old one.

5.1 Short-term stability study

For the short-term stability study, samples have been stored at -20 °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 below the CFPP of the material shows whether the solid paraffines created by freezing can be re-dissolved. The reference temperature was set to +4 °C. 12 samples per storage time were selected using a random stratified sampling scheme. From each storage temperature/time point combination, 6 samples were measured for the CFPP by EN 116 and 6 samples for the CP by ISO 3015. The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend over storage time. One sample stored at 60 °C for one week broke during transport, thus only 5 replicate analyses are available for this time/temperature combination.

The obtained data were evaluated individually for each temperature. As was the case for homogeneity testing, outlier testing was not useful for checking the CFPP data for consistency, as the results are rounded to full °C. The values obtained ranged from -8 to -9 °C, therefore clearly fulfilling the requirement for the method (only 1 out of 20 differences of two results larger than 1.76 °C). Results for CP were given with one digit behind the comma. These results were screened for outliers using the single and double Grubbs test and no outliers were detected on a 99 % confidence level.

The data were plotted against storage time and regression lines of CFPP or CP versus time were calculated. This regression is possible even with the data rounded to full °C. The slope of the regression lines was then tested for statistical significance (loss/increase due to shipping conditions). For all parameters, the slopes of the regression lines were not significantly different from 0 (on 99 % confidence level) for both -20 °C and +60 °C.

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

Measurand	Significance of the trend on a 99% confidence level	
	-20 ºC	+60 ºC
CFPP	no	no
CP	no	no

The mean values obtained for storage at +60 °C did not differ significantly (95 % confidence level) from those at -20 °C. This shows that both CFPP and CP are not affected by temperatures of -20 °C.

The material can be dispatched without further precautions under ambient conditions. The absence of a trend at +60 °C also indicates, based on the applicability of a 4 week +120 °F test, stability of the material for more than one year.

5.2 Long-term stability study

For the long-term stability study, samples have been stored at +18 °C for 0, 3, 6 and 9 months. The reference temperature was set to +4 °C. 12 samples per storage time were selected using a random stratified sampling scheme. From each time point, 6 samples were measured for the CFPP by EN 116 and 6 samples for the CP by ISO 3015. The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend over storage time.

As was the case for homogeneity testing, outlier testing was not useful for checking the CFPP data for consistency, as the results are rounded to full °C. The same test as for homogeneity was made, i.e. all possible $\binom{24}{2}$ combinations of two results of all data of the stability study were made 31 of the 276 combinations differed by more than 2 °C. The dataset was therefore worse than prescribed by the standard, but was deemed still suitable for evaluation. Results for CP were given with one digit behind the comma. These results were screened for outliers using the single and double Grubbs test and no outliers were detected on a 99 % confidence level.

Furthermore, the data were plotted against storage time and regression lines of CFPP and CP versus time were calculated. The slope of the regression lines was then tested for statistical significance (loss/increase due to storage conditions). For both parameters the slopes of the regression lines were not significantly different from 0 (on 99 % confidence level) for the tested temperature of +18 °C.

The results of the measurements are shown in Annex C. No technically unexplained outliers were observed and none of the trends was statistically significant on a 99 % confidence level for any of the temperatures. The material can therefore be stored at +18 °C.

A second set of data is available for CFPP from the stability monitoring of BCR-395. This material was certified in 1991. The stability tests consisted of 23 samples being tested using

IP309 performed in 2006. The results of this study are shown together with the certified value in Table 3 and demonstrate stability of the material.

Table 3: Certified value and stability monitoring result of BCR-395 [10]*. Uncertainty for the certification is the standard uncertainty (standard error of the mean of the 26 laboratory means). In the stability monitoring, 23 times the value 6 was obtained and the uncertainty given is the standard uncertainty for 23 measurements according to equation 3.*

	Certification 1991 [°C]	Stability monitoring 2007 [°C]
CFPP	-5.8 ± 0.2	-6.0 ± 1.2

5.3 Estimation of uncertainties

Due to the intrinsic variation of measurement results no study can rule out degradation of materials completely, even in the absence of statistically significant trends. It is therefore necessary to quantify the potential degradation that could be hidden by the method repeatability, i.e. to estimate the uncertainty of stability. This means, even under ideal conditions, the outcome of a stability study can only be "degradation is 0 ± x % per time".

Uncertainties of stability during dispatch and storage were estimated as described in [16] for each analyte. For this approach, the uncertainty of the linear regression line with a slope of zero is calculated. The uncertainty contribution (u_{lts}) is then calculated as the product of the chosen shelf life and the uncertainty of the regression lines as

$$u_{lts} = \frac{RSD}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot t_{sl} \qquad \text{Eq. (5)}$$

RSD	relative standard deviation of all results of the stability study
$\bar{x}$	mean results for all time points
x_i	individual time points
t_{sl}	proposed shelf life (36 months at +18 °C in this case)

A second estimate for the stability during storage was obtained from the stability monitoring following the same principle as described in [16]. The best estimate for the change over 16 years is [(-5.8) – (-6.0)]/16 = 0.013 °C per year. The uncertainty of this degradation is the combined uncertainty as obtained from the certification study and from the stability monitoring. Using the standard uncertainties from Table 3, a value of 1.21 °C is obtained for the period of 16 years. This amounts to an uncertainty of 0.075 °C per year.

The following uncertainties were estimated:

- u_{sts} the uncertainty of degradation during dispatch. This was estimated from the +60 °C studies for a time of 0.25 months (1 week). The uncertainty therefore describes the possible change during a dispatch at +60 °C lasting for one week.
- u_{lts} the stability during storage. This uncertainty contribution was estimated from the +18 °C study as well as from the stability monitoring data. The uncertainty contribution therefore describes the possible degradation for 36 months (proposed shelf life) at +18 °C.

The results of these evaluations are summarised in Table 4.

Table 4: Uncertainties of stability during dispatch and storage. u_{sts} was calculated for a temperature of +60 °C and 1 week; u_{lts} was calculated for a storage of 3 years at +18 °C.

	u_{sts} [°C]	u_{lts} [°C]	
		isochronous study	stability monitoring
CFPP	0.055	2.50	0.23
CP	0.039	1.33	not applicable

It should be noted that u_{sts} for CFPP cannot be precisely estimated: all but two results were -9 °C and only two results were -8 °C. The standard deviation of results, which forms the bases for the uncertainty estimation, therefore stems from not normally distributed data. However, the value is sufficiently small to be negligible compared to the other uncertainties.

The uncertainty of stability during dispatch is negligible even at +60 °C. Therefore the material can be transported at ambient conditions without special precautions. For CFPP, the uncertainty estimate from the stability monitoring will be used, as the long duration of the time for stability monitoring allows setting stricter limits for the uncertainty of stability.

After the certification campaign, the material will be subjected to IRMM's regular stability monitoring programme to control its further stability.

5.4 Repeated use of the material

The possibility to re-use the sample was tested. 10 replicate analyses of CP and CFPP were performed on the same sample, i.e. the sample was re-heated after each plugging/cloud formation before the next replicate was performed. Measurements were performed by EN 116 and ISO 3015.

All results were within 1 °C and hence within the expected variation. This indicates that a sample can be used several times.

6 Characterisation

The certified value should be as widely applicable as possible. Therefore, it was decided to apply as many technically equivalent methods as possible. Absence of difference between 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: ASTM D6371 and EN 116 either with manual or automated equipment for CFPP; ASTM D2500 and ISO 3015 (or EN 23015) either with manual or automated equipment for CP.

The material characterisation was based on an intercomparison of expert laboratories, i.e. the CFPP and CP of the material was determined in different laboratories to demonstrate the absence of a measurement bias. Due to the nature of the analytes however, all participants used the same measurement approach method for the measurements. This approach aims at randomisation of laboratory bias, which reduces the combined uncertainty.

6.1 Selection of participants

For the characterisation exercise of CFPP, 13 laboratories supposed to deliver 17 datasets by various methods were selected, whereas for CP 13 laboratories delivering 16 datasets were chosen. In both cases, selection was based on criteria that comprised both technical competence and quality management aspects. Participants had to behold ISO 17025 accreditation for the determination of CFPP and/or CP. In addition, they had to demonstrate their proficiency in the determination of CFPP and/or CP providing results for

intercomparison exercises or method validation reports. Laboratories could submit more than one dataset (e.g. for manual and automated methods).

Care was taken to include both manual and automated equipment as well as laboratories following the various apparently equivalent procedures. Laboratories performed the measurements as follows:

CFPP:

- EN116: 8 automated; 2 manual
- ASTM D6371: 3 automated; 3 manual

CP:

- ISO 3015/EN 23015: 8 automated; 3 manual
- ASTM D2500: 1 automated; 4 manual

6.2 Study setup

Each laboratory received 6 units of ERM-EC395k and was requested to provide 6 independent results, one per unit. The units for material characterisation were selected using a random stratified sampling scheme and covered the whole batch. The sample preparations and measurements had to be spread over three days (2 samples per day) to ensure intermediate precision conditions.

Each participant received a blinded quality control (QC) sample. This sample was for the determination of CFPP either BCR-395 [10], or a certified reference material diesel (PAC GmbH, Part No: 01000-309-51, Lot No: 1040, re-ampouled at IRMM) and for the determination of CP a certified reference material diesel (PAC GmbH, Part No: 01000-815-51, Lot No: 1043, re-ampouled at IRMM) The results for the QC samples have been used to support the evaluation of the characterisation results.

Laboratories were not requested to submit measurement uncertainties, as the accuracy of the methods is described in the respective standards. However, they had to send detailed description of their equipment to allow checking whether it indeed complied with the specifications of the standard. Furthermore, they were asked to state the standard deviation from their routing quality control chart.

6.3 Methods used

All laboratories used the same method either EN116 or ASTM D6371 for CFPP or ISO 3015/EN23015 or ASTM D2500 for CP.

6.4 Evaluation of results

The characterisation campaign resulted in 16 datasets each for CFPP and CP. The method used by each laboratory is shown in Annex D. All individual results of the participants are displayed in tabular and graphical form in Annex E.

6.4.1 Technical evaluation

Two laboratories (Lab 1 and Lab 9) for CFPP and three laboratories (Lab 1, Lab 5 and Lab 6) for CP performed tests both according to the EN/ISO as well as the ASTM method (see Annex D). The laboratories were asked whether the equipment used for the two standards was the same. If this was the case (i.e. Lab 9c for CFPP, and Lab 1 and Lab 6 for CP), the results from the laboratory were pooled, as the variation between laboratories was larger

than the variation within laboratories (see Table 5). In this way, the laboratory bias from these laboratories does not contribute more than the one of the others.

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:

- compliance with the analysis protocol: sample preparations and measurements performed on three days,
- compliance of the equipment with the specifications given in the standards (see also Annex D),
- method performance: agreement with the reproducibility limits given in the standard. For this, the differences of all possible combinations of each laboratory were calculated and the fraction of differences above the repeatability and reproducibility limits were determined.
- absence of bias, i.e. agreement of the measurement results with the assigned value of the QC sample within the uncertainties given for the QCM and the measurement uncertainties as estimated according to 1.2.

All laboratories complied with the analysis protocol and all equipments were in compliance with the standards. One laboratory had reported a too low temperature of the cooling bath (-40 °C rather than -34 °C). This laboratory confirmed that this was the setting of the cryostat and that the bath temperature was -34 °C and therefore within specifications. This value was retained.

A visual inspection of the data (see Annex E) shows that there is no difference between manual and automated methods and between results from ASTM and EN or ISO, confirming the technical equivalence of the standards. Therefore, results from all methods were pooled.

Method performance for nearly all laboratories was in agreement with the repeatability limits, despite the fact that the measurements were performed on three days. Even for those laboratories where the values were above these limits, the criterion for reproducibility was met. Therefore all datasets passed this criterion. Some specific observations were made:

CFPP:

Laboratory 1 reported CFPP values below those from other laboratories. The laboratory stated that it tends to have slightly negative z-scores (around -1) in intercomparisons. These low values were therefore not unusual and within the normal statistical variation of the method. The dataset result was retained.

Laboratory 9 used the same equipment for the manual determination of CFPP for ASTM and EN methods. The results were therefore pooled to form a single dataset (coded 9c)

Laboratory 11 reported an average CFPP value above the CP value (CP: -9.3 °C; CFPP: -7 °C). This is impossible, as precipitates must form first and then can block the filter. The results were therefore discarded.

Laboratory 13 reported for the QC sample of CFPP a value of -9 °C rather than the -20 ± 3.3 °C stated on the certificate. The laboratory confirmed that this was not a transcription error (i.e. -9 reported instead of -19). This dataset was therefore rejected, although the results on ERM-FC395k were in line with the other results.

Thus the final number of datasets accepted for CFPP was 13.

CP:

Laboratory 1 used the same equipment for the manual determination of CFPP for ASTM and EN methods. The results were therefore pooled to form a single dataset.

Laboratory 6 used the same equipment for the manual determination of CFPP for ASTM and EN methods. The results were therefore pooled to form a single dataset.

Laboratory 11 reported an average CFPP value above the CP value (CP: -9.3 °C; CFPP: -7 °C). This is impossible, as precipitates must form first and then can block the filter. The results were therefore discarded.

Thus the final number of datasets accepted for CP was 13.

6.4.2 Statistical evaluation

The datasets accepted on technical grounds were tested for normality of dataset means using 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 deviation within (s_{within}) and between ($s_{between}$) laboratories were calculated using one-way ANOVA. The results of these evaluations are shown in Table 5.

Table 5: Statistical evaluation of the technically accepted datasets for CFPP and CP. p: number of technically valid datasets.

Measurand	p	Outliers		Normally distributed	Statistical parameters			
		Means	Variances		Average [°C]	s [°C]	$s_{between}$ [°C]	s_{within} [°C]
CFPP	13	none	none	yes	-7.87	1.62	1.65	0.67
CP	13	none	yes	yes	-7.19	0.54	0.51	0.57

Laboratory 13 was flagged as an outlier of variance on a 99 % level for CP. This is not an exclusion criterion in itself. As the results agree with the repeatability requirements of the standard, the values were retained.

It is interesting to note that the standard deviation of laboratory means for CFPP is smaller than the between-laboratory standard deviation. This is most likely a statistical artefact. The laboratory averages follow normal distributions. None of the data contains outlying means and variances. The datasets are therefore consistent and the mean of laboratory means is a good estimate of the true value. For CFPP, 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 standard error of the mean of laboratory means ($s/\sqrt{p}$) was adopted as uncertainty of characterisation (u_{char}).

7 Value Assignment

Based on the results, certified values could be assigned:

Certified values are values that fulfil the highest standards of accuracy. Procedures at IRMM 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] must be established.

7.1 Certified values and their uncertainties

The unweighted means of the means of the accepted datasets as shown in Table 5 were assigned as certified values for the parameters.

The assigned uncertainties consist of uncertainties related to characterisation, u_{char} (see Section 6), potential between-unit inhomogeneity, u_{bb} (see Section 4) and potential degradation during transport (u_{sts}) and long-term storage, u_{lts} (see Section 5). These different contributions were combined to estimate the expanded, relative uncertainties of the certified values ($U_{CRM,rel}$) with a coverage factor k as

$$U_{\text{CRM,rel}} = k \cdot \sqrt{u_{\text{char,rel}}^2 + u_{\text{bb,rel}}^2 + u_{\text{sts,rel}}^2 + u_{\text{lts,rel}}^2}$$

- u_{char} was estimated as described in section 6.4.2
- u_{bb} was estimated as described in section 4.1
- u_{sts} was estimated as described in section 5.3
- u_{lts} was 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-FC395k

Property	Certified value [°C]	u_{char} [°C]	u_{bb} [°C]	u_{sts} [°C]	u_{lts} [°C]	U_{CRM} (k=2) [°C]
CFPP	-7.9	0.45	0.61	0.055	0.23	1.6
CP	-7.3	0.15	0.66	0.039	1.33	3.0

8 Metrological traceability and commutability

8.1 Metrological traceability

Identity

CFPP and CP are method-defined measurands and can only be obtained by following the procedure specified in EN116 or ASTM D6371 (CFPP) and ISO 3015/EN23015 or ASTM D2500 (CP). Adherence to these procedures was confirmed by agreement of the laboratories' results with the assigned values for the CRMs that were used as quality control samples. The assigned values are therefore operationally defined by *method*.

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 SI. Consistency in the interlaboratory comparison demonstrates that all relevant input factors were covered. 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 are selecting specific (or specific groups) of analytes from the sample for the subsequent steps of the 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 the 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 nowadays summarised in a concept called 'commutability of a reference material'. There are various definitions expressing this concept. For instance, the CSLI Guideline C-53A [17] 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, thus, is a crucial characteristic in case of the application of different measurement methods. When commutability of a CRM is not established in such cases, 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 calibrator.

As the material comes from an industrial, diesel producing plant, it is representative of other diesel samples.

9 Instructions for use

9.1 Storage conditions

The materials shall be stored at 18 °C ± 5 °C in the dark.

Repeated tests on the same sample showed no significant change of CP and CFPP within 10 consecutive measurements, indicating that samples can be re-used. However, 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 of opened samples.

9.2 Safety and protection for the environment

The usual hazard and precautionary phrases for diesel apply:

H350: May cause cancer

P201: Obtain special instructions before use.
P202: Do not handle until all safety precautions have been read and understood.
P281: Use personal protective equipment as required.
P308+P313: If exposed or concerned: Get medical advice/attention.
P405: Store locked up.

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 or mixing is necessary.

Minimum sample intake

The minimum sample intake representative for CFPP and CP is 50 mL.

9.4 Use of the certified value

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

Comparing an analytical result with the certified value

A result is unbiased if the expanded uncertainty of measurement and certified value covers the difference between the certified value and the measurement result (see also ERM Application Note 1, www.erm-crm.org [18]).

For assessing the method performance, the measured values of the CRMs are compared with the certified values. The procedure is described here in brief:

- Calculate the absolute difference between mean measured value and the certified value (Δ_m).
- Combine measurement uncertainty (u_m) with the uncertainty of the certified value (u_{CRM}): $u_\Delta = \sqrt{u_m^2 + u_{CRM}^2}$
- Calculate the expanded uncertainty (U_Δ) from the combined uncertainty (u_Δ) using an appropriate coverage factor, corresponding to a level of confidence of approximately 95 %.
- If $\Delta_m \leq U_\Delta$ then there is no significant difference between the measurement result and the certified value, at a confidence level of about 95 %.

Use in quality control charts

The material can be used for quality control charts. Different CRM-units will give the same result as heterogeneity was included in the uncertainties of the certified values.

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Annexes

Annex A: Results of the homogeneity measurements

Annex B: Results of the short-term stability measurements

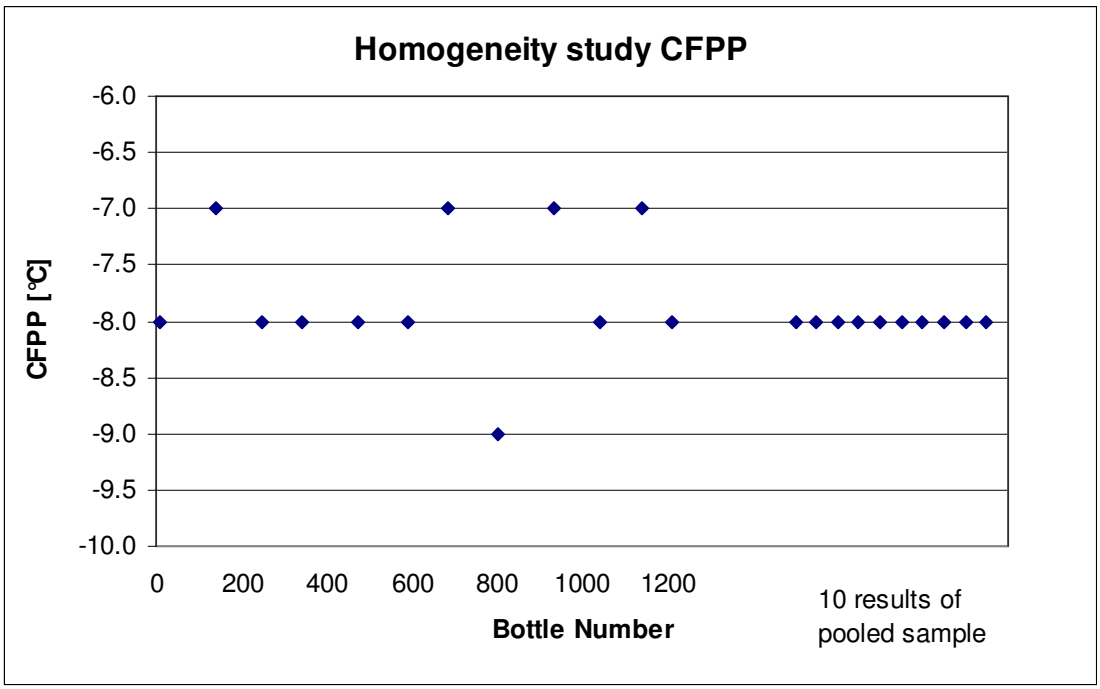
Annex C: Results of the long-term stability measurements

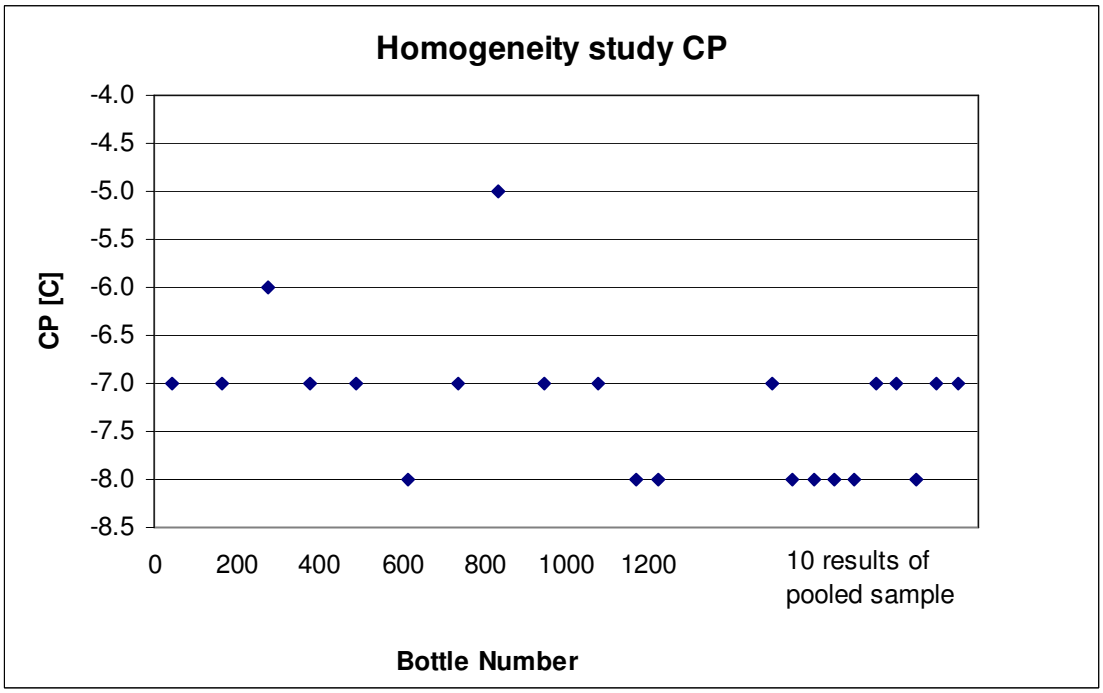
Annex D: Summary of methods used in the characterisation

Annex E: Results of the characterisation measurements

Annex A

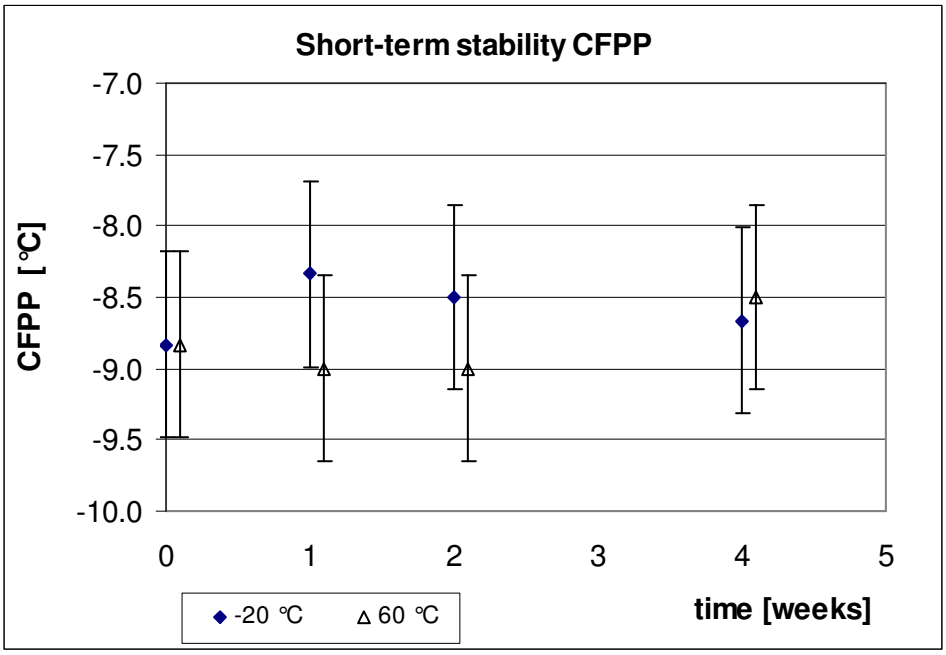
Results of the homogeneity study

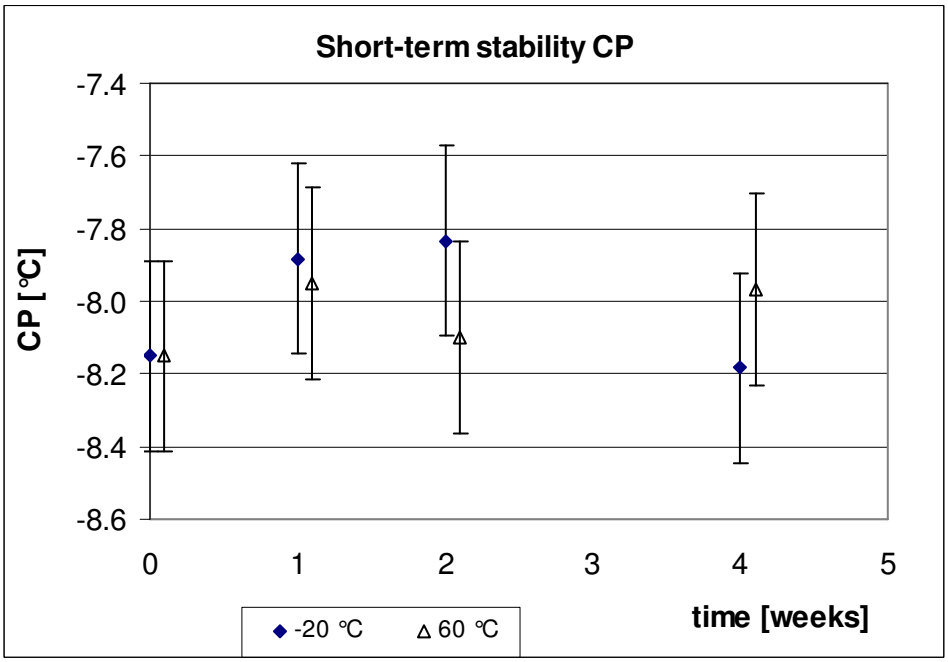




Annex B

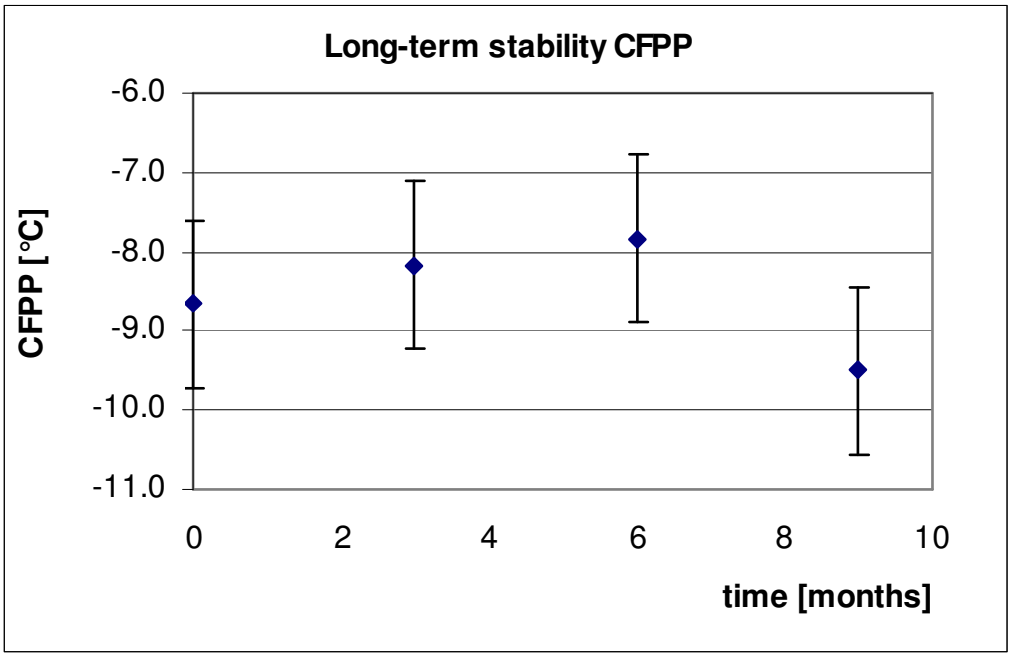
Results of the short-term stability study. For CP, error bars are 95 % confidence intervals of the mean based on the within-group standard deviation as obtained by single-factor ANOVA. For CFPP, data were given as full °C so ANOVA was impossible. Therefore, error bars are 95 % confidence intervals of the mean based on a repeatability standard deviation of 0.62 k (from the standard).

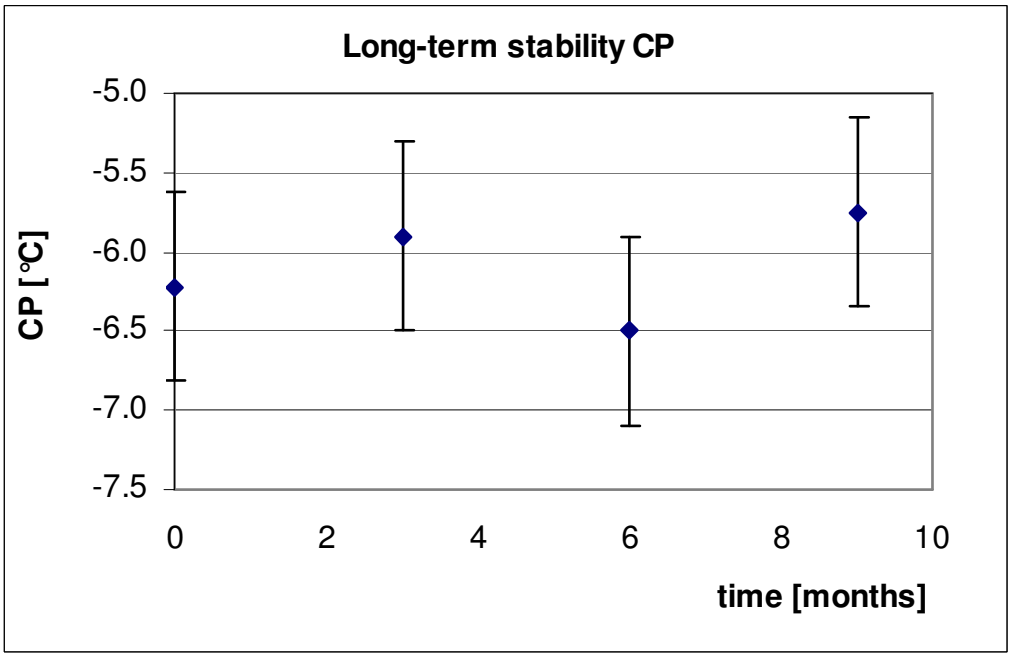




Annex C

Results of the long-term stability study. Error bars are 95 % confidence intervals of the mean based on the within-group standard deviation as obtained by single-factor ANOVA.





Annex D

Methods used for certification of CFPP

LAB. CODE	Standard	M=man. A=autom.	Instrument	Thermometer		Filter paper	Cooling	
				Specs.	Latest calib.		T cooling bath [°C]	Start T [°C]
LAB 1a	ASTM D 6371	A	HERZOG MP 842	ASTM 6C	Jan 2010	Machery-Nagel 616 1/4, Ø 185 mm	-34	20
LAB 1b	EN 116	A	HERZOG HCP 842	ASTM 6C	Nov 2002	Machery-Nagel 616 1/4, Ø 185 mm	-34	20
LAB 2	EN 116	A	NORMALAB ANALIS NTL 450 TL A E06 A584.3	–	02/02/2011	Whatman No 3 (batch G11191081)	-34	0-10
LAB 3	EN 116	A	ISL CPP 97-2	IEC 751-Class A	27/04/2011	Whatman No 3 (1003-090)	-34	19.8-21.3
LAB 4	EN 116	A	HERZOG HCP 842	Pt-100	15/09/2011	Whatman No 3 (H71810031101)	-34	20
LAB 5	EN 116	M	ISL FPP-5Gs	ASTM 5C	13/11/2006	Whatman No 3	-34	0
LAB 6	ASTM D 6371	A	–	Pt 100	14/12/2010	Whatman No 4	-34	5-10
LAB 9a	EN 116	A	NORMALAB ANALIS NTL 450 TL A K07 607.9	Pt 100	15/07/2010	Filter-lab 1300 / 80 Batch 127 / 08	-34	5-10
LAB 9b	ASTM D 6371	A	NORMALAB ANALIS NTL 450 TL A L06 A591.0	Pt 100	15/07/2010	Filter-lab 1300 / 80 Batch 127 / 08	-34	5-10
LAB 9c	EN 116	M	ANALIS P 592 57629	ASTM 5C	24/03/2011	Filter-lab 1300 / 80 Batch 127 / 08	-33.5	10
	ASTM D 6371				28/09/2010			
LAB 10	EN 116	A	ISL CPP-97 2	Pt-100 (Model MP2503)	28/03/2011	Whatman No 3 (1003-055)	-34.3	5
LAB 11	ASTM D 6371	M	–	ASTM 5C	06/06/2011	Advantec No 2	-34	1
LAB 12	EN 116	A	OILLAB 100, LINETRONIC SA	IEC 751 class A	25/10/2011	Whatman No 3 (J11588970)	-34	5
LAB 13	ASTM D 6371	M	–	ASTM 6C	10/10/2011	P4, FC000968	-34	5
LAB 14	EN 116	A	ISL CPP 97-2	–	01/03/2012	Albet LabScience DF 597150	-35	5

– : no information provided

Methods used for certification of CP

LAB. CODE	Standard	M=man. A=autom.	Instrument	CP detection (for automated)	Thermometer (for manual)		T bath [°C] (for manual)	
					Specs.	Latest calib.	Bath 2	Bath 3
LAB 1	EN 23015 ASTM D 2500	A	ISL CPP 5Gs	reflection	–	–	–	–
LAB 3	EN 23015	A	ISL CPP 97-2	reflection	–	–	–	–
LAB 4	ISO 3015	A	Herzog HCP 852	optical detection system CCD	–	–	–	–
LAB 5a	ISO 3015	A	ISL CPP 5Gs	reflection	–	–	–	–
LAB 5b	ISO 3015	M	–	–	ASTM 5C	01/04/2010	-17	-33
LAB 6	ISO 3015 ASTM D 2500	M	–	–	ASTM 5C	01/09/2011	-17	-33
LAB 7	ISO 3015	A	Herzog HCP 852	reflection	–	–	–	–
LAB 8	ISO 3015	M	–	–	ASTM 5C/IP1C	18/03/2010	-18	-33
LAB 9	ASTM D 2500	M	–	–	ASTM 5C	28/09/2010	-18.3	-33.5
LAB 10	EN 23015	A	ISL CPP 97-2	–	–	–	–	–
LAB 11	ASTM D 2500	M	–	–	ASTM 5C	06/06/2011	-17	-32
LAB 12	EN 23015	A	Herzog MC 840	reflection	–	–	–	–
LAB 13	ASTM D 2500	M	–	–	ASTM 6C	05/08/2011	-18	-33
LAB14	ISO 3015	A	ISL CPP 97-2	reflection	–	–	–	–

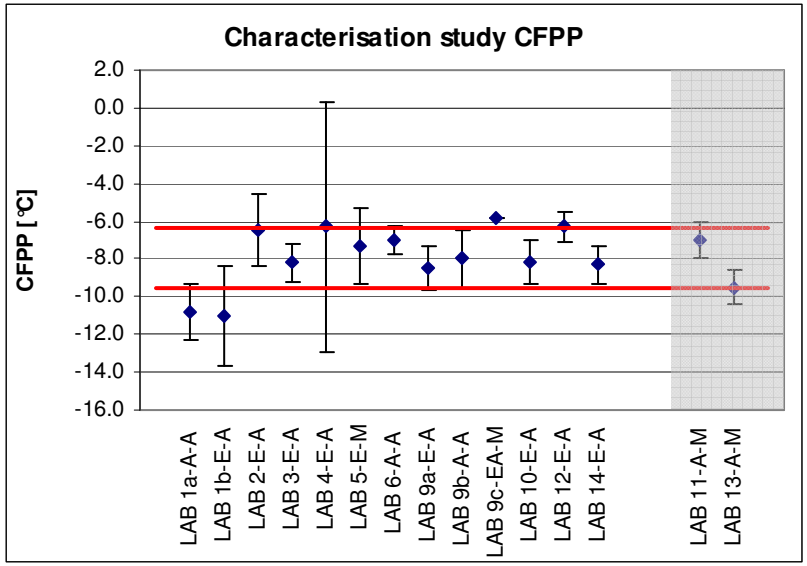
– : no information provided

Annex E

Results of the characterisation measurements for CFPP

Lab. code	Measurement results [°C]												Average [°C]	U* [°C]
	1	2	3	4	5	6	7	8	9	10	11	12		
LAB 1a	-10	-12	-10	-11	-11	-11	–	–	–	–	–	–	-10.8	1.5
LAB 1b	-11	-12	-10	-10	-11	-12	–	–	–	–	–	–	-11.0	2.64
LAB 2	-6	-6	-7	-7	-6	-7	–	–	–	–	–	–	-6.5	1.8-2.0
LAB 3	-8	-8	-8	-9	-8	-8	–	–	–	–	–	–	-8.2	1.0
LAB 4	-7	-6	-7	-6	-6	-6	–	–	–	–	–	–	-6.3	6.6
LAB 5	-6	-8	-8	-8	-7	-7	–	–	–	–	–	–	-7.3	2
LAB 6	-7	-7	-7	-7	-7	-7	–	–	–	–	–	–	-7.0	0.6-0.8
LAB 9a	-9	-8	-9	-9	-7	-9	–	–	–	–	–	–	-8.5	1.16
LAB 9b	-8	-9	-8	-8	-7	-8	–	–	–	–	–	–	-8.0	1.56
LAB 9c	-5	-6	-6	-6	-6	-6	-5	-6	-7	-6	-5	-5	-5.8	–
LAB 10	-8	-9	-8	-7	-8	-9	–	–	–	–	–	–	-8.2	1.16
LAB 12	-7	-7	-6	-6	-6	-6	–	–	–	–	–	–	-6.3	0.8
LAB 14	-10	-8	-8	-8	-8	-8	–	–	–	–	–	–	-8.3	1.0
Results not used for certification														
LAB 11	-7	-8	-7	-6	-7	-7	–	–	–	–	–	–	-7.0	–
LAB 13	-9	-9	-10	-9	-10	-10	–	–	–	–	–	–	-9.5	–

*U was estimated as two times the standard deviation from the quality control chart



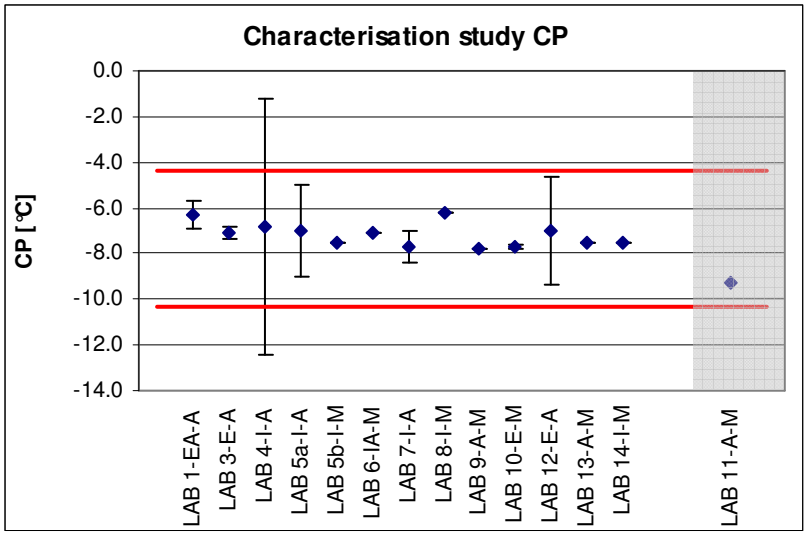
Error bars show the expanded uncertainties (2 times the standard deviation of the quality control chart as stated by the laboratories). Shaded results were not used for certification.

E-A: EN116-automated; E-M: EN116-manual; A-A: ASTM D6371-automatied; A-M: ASTM-D6371-manual; EA-M: EN116 and ASTM D6371 on the same manual instrument.

Results of the characterisation measurements for CP

LAB. CODE	Measurement results [℃]												Average [℃]	U* [℃]
	1	2	3	4	5	6	7	8	9	10	11	12		
LAB 1	-6.9	-5.7	-6.9	-6.6	-7.3	-7.0	-5.9	-5.9	-6.1	-5.5	-6.4	-5.6	-6.3	0.64
LAB 3	-7.1	-7.3	-7.1	-6.8	-6.8	-7.6	–	–	–	–	–	–	-7.1	0.28
LAB 4	-7	-6	-7	-7	-7	-7	–	–	–	–	–	–	-6.8	5.6
LAB 5a	-7	-7	-7	-6	-7	-8	–	–	–	–	–	–	-7.0	2
LAB 5b	-8	-8	-8	-7	-7	-7	–	–	–	–	–	–	-7.5	–
LAB 6	-7	-8	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7	-7.1	–
LAB 7	-7	-7	-8	-8	-8	-8	–	–	–	–	–	–	-7.7	0.7
LAB 8	-6	-6	-6	-7	-6	-6	–	–	–	–	–	–	-6.2	–
LAB 9	-8	-8	-8	-7	-8	-8	–	–	–	–	–	–	-7.8	–
LAB 10	-7.8	-7.0	-7.6	-7.6	-8.1	-8.1	–	–	–	–	–	–	-7.7	0.12
LAB 12	-7	-7	-7	-7	-7	-7	–	–	–	–	–	–	-7.0	2.4
LAB 13	-6	-6	-9	-7	-9	-8	–	–	–	–	–	–	-7.5	–
LAB 14	-7.6	-7.6	-8.4	-7.2	-7.5	-8.5	–	–	–	–	–	–	-7.8	–
Results not used for certification														
LAB 11	-9	-10	-9	-9	-9	-10	–	–	–	–	–	–	-9.3	–

*U was estimated as two times the standard deviation from the quality control chart as stated by the laboratories



Error bars show the expanded uncertainties (2 times the standard deviation of the quality control chart). Shaded results were not used for certification.

E-A: EN23015-automated; E-M: EN23015-manual; I-A: ISO 3015-automated; I-M: ISO 3015-manual; A-A: ASTM D2500-automated; A-M: ASTM-D2500-manual EA-A: EN23015 and ASTM D2500 on the same automated instrument; IA-M: ISO 3015 and ASTM D2500 on the same manual instrument.

European Commission

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Abstract
This report describes the production of ERM-FC395k, a gas oil material certified for cold filter plugging point (CFPP) and cloud point (CP).

The material has been produced following ISO Guide 34:2009 .
A mixture of hydrotreated straight-run distillates and cracked diesel fractions without flow improvers and fatty acid methyl esters was obtained. The material was ampouled in amber glass ampoules.
Between unit-heterogeneity has been quantified and stability during dispatch and storage have been assessed in accordance with ISO Guide 35:2006. Within-unit heterogeneity has been quantified to determine the minimum sample intake.
The material was characterised by an intercomparison among laboratories of demonstrated competence and adhering to ISO/IEC 17025 . Technically invalid results were removed but no outlier was eliminated on statistical grounds only.
Uncertainties of the certified values were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM), including uncertainties related to possible heterogeneity and instability and to characterisation.
The material is intended for the quality control and assessment of method each 27 mL of diesel performance. As any reference material, it can also be used for control charts or validation studies. The certified reference material (CRM) is available in sets of two glass ampoules containing closed under argon atmosphere. The contents of the two ampoules shall be mixed to obtain one sample of 50 mL.
The CRM has been accepted as European Reference Material (ERM®) after peer evaluation by the partners of the European Reference Materials consortium.

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