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# CERTIFICATION REPORT

# The certification of mass fraction of Solvent Yellow 124 in gas oil: ERM®-EF318k

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Abstract

This report describes the production of ERM®-EF318k, which is a matrix material certified for the mass fraction of Solvent Yellow 124, SY124. It is a remake of ERM-EF318, which is out of stock. This material was produced following ISO Guide 34:2009 and has been certified in accordance with ISO Guide 35:2006.

The starting materials were commercially available B0 gas oil (B0: without biodiesel) and SY124 produced as a CRM (ERM-AC316a). The material was prepared gravimetrically using calibrated balances and the mass fraction was confirmed by independent measurements. The solution of SY124 in gas oil was ampouled under argon atmosphere and stored at 18 °C in the dark.

Between-unit homogeneity was quantified and stability during dispatch and storage were assessed in accordance with ISO Guide 35:2006. The minimum sample intake was established based on the data available in the certification report of ERM-EF318.

The certified value was obtained from the gravimetric preparations, taking into account the purity of the base materials. The certified value was confirmed by HPLC-UV, i.e. Community Reference Method to analyse SY124, as an independent verification method (measurements were within the scope of accreditation to ISO/IEC 17025:2005).

The uncertainty of the certified value was calculated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM) and includes uncertainties related to possible inhomogeneity, instability and characterisation.

The material is intended for the quality control / assessment of method performance. As with any reference material, it can be used for establishing control charts or validation studies. The CRM is available in amber glass ampoules containing at least 4.2 mL of gas oil which were sealed under an atmosphere of argon. The minimum amount of sample to be used is 20 µL.

# CERTIFICATION REPORT

# The certification of mass fraction of Solvent Yellow 124 in gas oil: ERM®- EF318k

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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®-EF318k, which is a matrix material certified for the mass fraction of Solvent Yellow 124, SY124. It is a remake of ERM-EF318, which is out of stock. This material was produced following ISO Guide 34:2009 [1] and has been certified in accordance with ISO Guide 35:2006 [2].

The starting materials were commercially available B0 gas oil (B0: without biodiesel) and SY124 produced as a CRM (ERM-AC316a). The material was prepared gravimetrically using calibrated balances and the mass fraction was confirmed by independent measurements. The solution of SY124 in gas oil was ampouled under argon atmosphere and stored at 18 °C in the dark.

Between-unit homogeneity was quantified and stability during dispatch and storage were assessed in accordance with ISO Guide 35:2006 [2]. The minimum sample intake was established based on the data available in the certification report of ERM-EF318.

The certified value was obtained from the gravimetric preparations, taking into account the purity of the base materials. The certified value was confirmed by HPLC-UV, i.e. Community Reference Method [3,4] to analyse SY124, as an independent verification method (measurements were within the scope of accreditation to ISO/IEC 17025:2005 [5]).

The uncertainty of the certified value was calculated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM) [6] and includes uncertainties related to possible inhomogeneity, instability and characterisation.

The material is intended for the quality control / assessment of method performance. As with any reference material, it can be used for establishing control charts or validation studies. The CRM is available in amber glass ampoules containing at least 4.2 mL of gas oil which were sealed under an atmosphere of argon. The minimum amount of sample to be used is 20 µL.

The following value was assigned:

| | Mass fraction | |
|---|---|---|
| | Certified value [1] [mg/kg] | Uncertainty [2] [mg/kg] |
| Solvent Yellow 124 [3] (SY124) | 8.70 | 0.12 |

1) This value was derived from the gravimetric preparation of SY124 in gas oil. The certified value and its uncertainty are traceable to the International System of Units (SI).

2) The uncertainty is the expanded uncertainty of the certified value 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.

3) N-ethyl-N-[2-(1-isobutoxyethoxy)ethyl]-4-(phenylazo)aniline, CAS No 34432-92-3.

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## Glossary

| | |
|---|---|
| ANOVA | Analysis of variance |
| $b$ | Slope in the equation of linear regression $y = a + bx$ |
| CI | Confidence interval |
| C-KFT | Coulometric KFT |
| CRM | Certified reference material |
| EC | European Commission |
| EN | European norm (standard) |
| ERM$^®$ | Trademark of European Reference Materials |
| EU | European Union |
| FAME | Fatty Acid Methyl Ester |
| GUM | Guide to the Expression of Uncertainty in Measurements [6] |
| HPLC | High performance liquid chromatography |
| ISO | International Organization for Standardization |
| JRC | Joint Research Centre of the European Commission |
| $k$ | Coverage factor |
| KFT | Karl Fischer titration |
| $MS_{between}$ | Mean of squares between-unit from an ANOVA |
| $MS_{within}$ | Mean of squares within-unit from an ANOVA |
| $n$ | Number of replicates per unit |
| $N$ | Number of units analysed |
| QC | Quality control |
| rel | Index denoting relative figures (uncertainties etc.) |
| RSD | Relative standard deviation |
| $s$ | Standard deviation |
| $s_{bb}$ | Between-unit standard deviation; an additional index "rel" is added when appropriate |
| $s_{between}$ | Standard deviation between groups as obtained from ANOVA; an additional index "rel" is added as appropriate |
| SI | International System of Units |
| RM Unit | Reference Materials Unit of Directorate F |
| $s_{within}$ | Standard deviation within groups as obtained from ANOVA; an additional index "rel" is added as appropriate |
| $s_{wb}$ | Within-unit standard deviation |
| SY124 | Solvent Yellow 124 |

| | |
|---|---|
| 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-$\alpha$ and df degrees of freedom |
| $t_{sl}$ | Proposed shelf life |
| $t_{tt}$ | Chosen transport time |
| $u$ | Standard uncertainty |
| $U$ | Expanded uncertainty |
| $u^{*}_{bb}$ | Standard uncertainty related to a maximum between-unit inhomogeneity that could be hidden by method repeatability; an additional index "rel" is added as appropriate |
| $u_{bb}$ | Standard uncertainty related to a possible between-unit inhomogeneity; an additional index "rel" is added as appropriate |
| $u_c$ | Combined standard uncertainty; an additional index "rel" is added as appropriate |
| $u_{char}$ | Standard uncertainty of the material characterisation; an additional index "rel" is added as appropriate |
| $u_{CRM}$ | Combined standard uncertainty of the certified value; an additional index "rel" is added as appropriate |
| $U_{CRM}$ | Expanded uncertainty of the certified value; an additional index "rel" is added as appropriate |
| $u_{\Delta}$ | Combined standard uncertainty of measurement result and certified value |
| $u_{lts}$ | Standard uncertainty of the long-term stability; an additional index "rel" is added as appropriate |
| $u_{meas}$ | Standard measurement uncertainty |
| $U_{meas}$ | Expanded measurement uncertainty |
| $u_{rec}$ | Standard uncertainty related to possible between-unit inhomogeneity modelled as rectangular distribution; an additional index "rel" is added as appropriate |
| $u_{sts}$ | Standard uncertainty of the short-term stability; an additional index "rel" is added as appropriate |
| UV | Ultraviolet |
| $\Delta_{meas}$ | Absolute difference between mean measured value and the certified value |
| $v_{s,meas}$ | Degrees of freedom for the determination of the standard deviation $s_{meas}$ |
| $v_{MSwithin}$ | Degrees of freedom of MS$_{within}$ |

# 1   Introduction

## 1.1   Background

In Europe all gas oil and kerosene taxed at a rate different to the one used as propellant, i.e. road fuel, need to be marked [7]. To this end a range of national dyes has been used to facilitate the easy differentiation of the fuels with different prices in road side controls performed by many Member States. This practice has the objective to counteract fraudulent use of energy products exempt from excise duty or subject to a reduced excise duty rate.

In 1995, the European Commission introduced a common marker, the so called Euromarker, to facilitate harmonisation of excise duties on mineral oils [7]. In a study that lasted from 1996 to 2000, N-ethyl-N-[2-(1-isobutoxyethoxy)ethyl]-4-(phenylazo)aniline (Figure 1), also known as Solvent Yellow 124, CAS No 34432-92-3, was selected as most suitable candidate for such a common marker.

SY124 was introduced as common marker in the European Union on August 1, 2002 [8] with a lower marking level of 6 mg/L. In 2003 [9], the upper marking level was set at 9 mg/L.

**Figure 1**: Chemical formula of SY124.
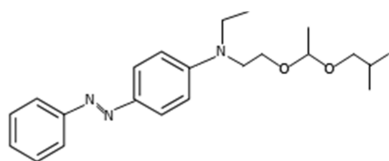


Following this decision, the Excise Duty Committee decided that the establishment of a community reference method was desirable, which should have a limit of quantification of not higher than 0.12 mg/L (2 % of the initial concentration or 50 times lower than the lower marking limit). A method validation study was performed in March 2004 [3, 4] and the method was found sufficiently accurate to detect potential fraud.

Two reference materials, one at the marking level of 6 mg/L (ERM-EF318) and one at the level of 0.12 mg/L (ERM-EF317) were produced to allow ongoing quality control by testing laboratories. Due to its high demand, ERM-EF318 was sold out. As a response to the requests for a replacement received from testing laboratories, a new batch of the high marking level material has been produced and was coded ERM-EF318k.

## 1.2   Choice of the material

ERM-EF318k is a gas oil matrix material produced in support of the Council Directive 95/60/EC [7] and replaces ERM-EF318. It was prepared using commercial B0 gas oil obtained from a petrol station and spiked with a Solvent Yellow 124 CRM (ERM-AC316a, LGC Standards, Teddington, UK [10]), to reach a SY124 mass fraction falling within the marking interval established by the Council Directive 95/60/EC.

## 1.3    Design of the CRM project

The selected starting materials and the preparation process followed resemble as much as possible the ones used in the preparation of ERM-EF318 in order to ensure the equivalence between the materials.

The certified value was obtained from the gravimetric preparation of the solution, taking into account the purity of SY124. Commercially available B0 gas oil was spiked with a SY124 CRM (ERM-AC316a) and therefore the purity stated on the certificate was used for the calculations. The certified value was confirmed by independent analyses performed by two laboratories using the Community Reference Method [3,4] to analyse SY124 in gas oil.

The short-term stability and homogeneity of the material were evaluated through dedicated studies. For the assessment of the long term stability of ERM-EF318k, data from the post-certification stability of ERM-EF318 were used since both materials were produced and stored in a similar way.

# 2    Participants

## 2.1    Project management and evaluation

European Commission, Joint Research Centre, Directorate F – Health, Consumers and Reference Materials, 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, Geel, BE

(accredited to ISO Guide 34 for production of certified reference materials, BELAC No. 268-RM)

## 2.3    Homogeneity study

Bildungs- und Wissenschaftszentrum der Bundesfinanzverwaltung, Wissenschaftliches Referat München, Markt-Schwaben, DE

(measurements under the scope of ISO/IEC 17025 accreditation, DAkkS No D-PL-11069-05-00)

## 2.4    Stability study

Bildungs- und Wissenschaftszentrum der Bundesfinanzverwaltung, Wissenschaftliches Referat München, Markt-Schwaben, DE

(measurements under the scope of ISO/IEC 17025 accreditation, DAkkS No D-PL-11069-05-00)

## 2.5    Characterisation

Bildungs- und Wissenschaftszentrum der Bundesfinanzverwaltung, Wissenschaftliches Referat München, Markt-Schwaben, DE

(measurements under the scope of ISO/IEC 17025 accreditation, DAkkS No D-PL-11069-05-00)

Laboratorium Douane & Accijnzen, Vilvoorde, BE

(measurements under the scope of ISO/IEC 17025 accreditation, BELAC No 426-TEST)

# 3 Material processing and process control

## 3.1 Origin and purity of the starting material

The starting material used for spiking, SY124, was a CRM certified for mass % [10]. The purity was obtained directly from the certificate of analysis (95.0 ± 1.2 mass %, $k$ = 2.15) and no further investigations were carried out.

The matrix is B0 winter type gas oil purchased in November 2017 in Aachen, DE.

## 3.2 Additional characterisation of the base materials

Prior to the processing of the material the purchased gas oil was further tested . The content of Fatty Acid Methyl Esters (FAMEs) was determined according to EN 14078:2014 [11] to confirm that the matrix was free of biodiesel. The density of the gas oil was measured following ISO 12185:1996 method [12].

The FAME content in the gas oil was <0.05 % (v/v) which is the lowest reported value by EN 14078:2014 standard. Therefore it was considered that the gas oil was truly B0 type gas oil. The density at 15 °C was reported to be 833.4 kg/m$^3$.

The absence of SY124 in the gas oil was confirmed by the Belgian Customs Laboratory, Laboratorium Douane & Accijnzen, after analysing two independent samples of the gas oil following the Community Reference Method for the analysis of SY124.

Water measurements in the gas oil were carried out in duplicate by coulometric Karl-Fischer titration, C-KFT. The water content was under the 200 mg/kg limit stablished in EN 590 [13]. This standard stablishes the requirements, test methods and threshold values for automotive gas oil in the EU and other European countries.

## 3.3 Processing

The gas oil was stored at room temperature and in the dark until processing. On the other hand SY124 (ERM-AC316a) was stored in a cool room at 4 °C in the dark following the instructions of the certificate of analysis. It was left to equilibrate to room temperature prior to its use.

A stock solution of 580 mg/kg SY124 in B0 gas oil was prepared gravimetrically using a Mettler Toledo XP504 (Mettler Toledo, Columbus, US) balance by mixing SY124 and B0 gas oil. The solution was mixed in the dark for an hour by means of a magnetic stirrer.

The final solution at the targeted mass fraction was prepared gravimetrically using a Sartorius FCG64EDE-H balance (Sartorius GmbH, Göttingen, DE) by further mixing the whole content of the stock solution with blank gas oil in a 20 L polyethylene drum.

The final solution was mixed by means of a magnetic stirred for an hour before ampouling. To remove most of the oxygen from the amber glass ampoules, they were flushed with argon over the headspace after filling with gas oil. The ampoules were flame-sealed directly after filling and flushing. The ampouling was performed on a ROTA automatic ampouling machine, model R910/PA (ROTA Verpackungstechnik GmbH & Co.KG, Wehr, DE). The 5 mL amber

glass ampoules were filled with 4.2 mL of gas oil. In total, 3000 ampoules were filled and labelled in fill-order so that each unit is associated with an unique identification number.

## 3.4    Process control

All ampoules produced were checked for leaks. The filling sequence was checked for a potential trend during the homogeneity and short-term stability studies. A significant trend was detected at a 95 % confidence level for the filling sequence of SY124 mass fraction and it was taken into account for the estimation of the uncertainty.

After processing, six units were selected randomly and the water content was analysed using C-KFT. The measured water content was below 200 mg/kg in all units. This quality criterion was predefined following the limits for water established in EN 590 [13].

# 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.

The within-unit inhomogeneity does not influence the uncertainty of the certified value when the minimum sample intake is respected, but determines the minimum size of an aliquot that is representative for the whole unit. The minimum samples intake has been stablished based on the outcome of the certification of the previous material, ERM-EF318, and confirmed in different studies during the preparation of ERM-EF318k.

## 4.1    Between-unit homogeneity

The between-unit homogeneity was evaluated to ensure that the certified value of the CRM is valid for all units of the material, within the stated uncertainty.

The number of units selected corresponds to approximately the cube root of the total number of units produced. 15 units were selected using a random stratified sampling scheme covering the whole batch for the between-unit homogeneity test. For this, the batch, 3000 units, was divided into 15 groups (with a similar number of units) and one unit was selected randomly from each group. Three independent samples were taken from each selected unit, and analysed by HPLC-UV (Community Reference Method to analyse SY124). 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.

Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence. Some significant (95 % confidence level) trends in the analytical sequence and filling sequence were visible, pointing at a changing parameter, e.g. a signal drift in the analytical system. The correction of biases, even if they are statistically not significant, was found to combine the smallest uncertainty with the highest probability to cover the true value [14]. Correction of trends is therefore expected to improve

the sensitivity of the subsequent statistical analysis through a reduction in analytical variation without masking potential between-unit heterogeneities. As the analytical sequence and the unit numbers were not correlated, trends significant on at least a 95 % confidence level were corrected as shown below:

$$x_{i\_corr} = x_i - b \cdot i$$  **Equation 1**

$b$ = slope of the linear regression

$i$ = position of the result in the analytical sequence

The trend-corrected dataset was assessed for consistency using Grubbs outlier tests at a confidence level of 99 % on the individual results and on the unit means. No outliers were found.

Quantification of between-unit inhomogeneity was undertaken by analysis of variance (ANOVA), which separates the between-unit variation ($s_{bb}$) from the within-unit variation ($s_{wb}$). The latter is equivalent to the method repeatability if the individual samples were representative for the whole unit.

Evaluation by ANOVA requires mean values per unit, which follow at least an unimodal distribution and results for each unit that follow an unimodal distribution with approximately the same standard deviations. The distribution of the mean values per unit was visually tested using histograms and normal probability plots. Too few data are available for the unit means to make a clear statement of the distribution. Therefore, it was checked visually whether all individual data follow a unimodal distribution using histograms and normal probability plots. Minor deviations from unimodality of the individual values do not significantly affect the estimate of between-unit standard deviations. The results of all statistical evaluations are given in Table 1.

**Table 1:** Results of the statistical evaluation of the homogeneity studies

| Measurand | Trends (before correction)* | | Outliers** | | Distribution | |
|---|---|---|---|---|---|---|
| | Analytical sequence | Filling sequence | Individual results | Unit means | Individual results | Unit means |
| SY124 | yes | yes | None | None | normal unimodal | normal unimodal |

*  95 % confidence level

** 99 % confidence level (after trend correction)

It should be noted that $s_{bb,rel}$ and $s_{wb,rel}$ are estimates of the true standard deviations and are therefore subject to random fluctuations. Therefore, the mean square between groups ($MS_{between}$) can be smaller than the mean squares within groups ($MS_{within}$), 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.* [15]. $u^*_{bb}$ is comparable to the LOD of an analytical method, yielding the maximum inhomogeneity that might be undetected by the given study setup.

Method repeatability ($s_{wb,rel}$), between–unit standard deviation ($s_{bb,rel}$) and $u^*_{bb,rel}$ were calculated as:

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$$s_{wb,rel} = \frac{\sqrt{MS_{within}}}{\overline{y}}$$

**Equation 2**

$$s_{bb,rel} = \frac{\sqrt{\dfrac{MS_{between} - MS_{within}}{n}}}{\overline{y}}$$

**Equation 3**

$$u^*_{bb,rel} = \frac{\sqrt{\dfrac{MS_{within}}{n}} \sqrt[4]{\dfrac{2}{v_{MSwithin}}}}{\overline{y}}$$

**Equation 4**

$MS_{within}$     mean of squares within-unit from an ANOVA

$MS_{between}$     mean of squares between-unit from an ANOVA

$\overline{y}$     mean of all results of the homogeneity study

$n$     mean number of replicates per unit

$v_{MSwithin}$     degrees of freedom of $MS_{within}$

The regression analyses performed to evaluate potential trends showed a trend in the filling sequence at 95 % confidence level. In this case the uncertainty was also assessed estimating $u_{rec}$, using a rectangular distribution between the highest and the lowest unit average. The corrected relative uncertainty is given in:

$$u_{rec} = \frac{|highest\ result - lowest\ result|}{2 \cdot \sqrt{3} \cdot \overline{y}}$$

**Equation 5**

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

**Table 2:** Results of the homogeneity study

| Measurand | $s_{wb,rel}$ [%] | $s_{bb,rel}$ [%] | $u^*_{bb,rel}$ [%] | $u_{rec,rel}$ [%] | $u_{bb,rel}$ [%] |
|---|---|---|---|---|---|
| SY124 | 0.18 | 0.19 | 0.05 | 0.25 | 0.25 |

The homogeneity study showed no outlying unit means. A trend in the filling sequence was found. The inhomogeneity as quantified as $u_{rec}$ is still sufficiently small to make the material useful. Therefore, $u_{rec}$ was used as estimate of $u_{bb}$.

## 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.

The material is a true solution and is not expected to have any relevant inhomogeneity. The minimum sample intake established during the ERM-EF318 certification was 20 µL, which is also the sample intake set in the Community Reference Method to analyse SY124. Since ERM-EF318k is a remake of ERM-EF318 and the same analytical method is used, it is assumed that samples ≥20 µL are homogeneous. This assumption was confirmed by the homogeneity, stability and characterisation studies, where sample intakes as low as 20 µL were found to give acceptable repeatability, demonstrating that there is no intrinsic inhomogeneity or contamination at a sample intake of 20 µL.

# 5   Stability

Time, temperature and light (including UV radiation) were regarded as the most relevant influences on the stability of the materials. The influence of UV and 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 units are to be transported without any additional cooling.

The stability studies were carried out using an isochronous design [16]. In this approach, ERM-EF318k units were stored for a particular length of time at different temperature conditions. Afterwards, the units were moved to conditions where further degradation can be assumed to be negligible (reference conditions). At the end of the isochronous storage, the units were 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 long-term stability of the material was assessed using post-certification stability data from ERM-EF318. Both materials were prepared gravimetrically and using similar base materials, commercially available winter type B0 gas oil and pure SY124. Since all the base materials are synthetic materials produced in a very reproducible manner it is expected that long-term stability data from ERM-EF318 can be reliably extrapolated to ERM-EF318k.

## 5.1   Short-term stability study

During the short-term stability study of the previous CRM, ERM-EF318, neither freezing (-20°C) nor exposure to 60 °C for four weeks affected the stability of the material. Hence, it was expected that ERM-EF318k would be stable at these conditions as well. Since high temperatures are more likely to happen during the shipment, the stability at high temperature was tested again for the present material.

For the short-term stability study of ERM-EF318k, units were stored at 60 °C for 0, 1, 2 and 4 weeks. The reference temperature was set at 18 °C. 2 units per storage time were selected using a random stratified sampling scheme. From each unit, 2 samples were measured with the Community Reference Method to analyse SY124. The measurements were performed under repeatability conditions, and a randomised sequence was used to differentiate any potential analytical drift from a trend over storage time.

The data for the short-term stability at 60 °C were evaluated. The results were screened for outliers using the single and double Grubbs test on a confidence level of 99 %. One outlying individual result was found (Tabele 3). As no technical reason for the outliers could be found all data were retained for statistical analysis.

In addition, the data were evaluated against storage time, and regression lines of mass fraction versus time were calculated, to test for potential increases/decrease of the measurand mass fraction due to shipping conditions. The slope of the regression line was tested for statistical significance. The trend was not statistically significant at a 95 % confidence level at the test temperature, 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 3.

**Table 3:** Results of the short-term stability tests

| Measurand | Number of individual outlying results* | Significance of the trend ** |
|---|---|---|
| | 60 ºC | 60 ºC |
| SY124 | 1 statistical outlier (retained) | no |

   * 99 % confidence level

  ** 95 % confidence level

A statistical outlier was detected for SY124 but it was retained for the estimation of $u_{sts}$. None of the trends was statistically significant on a 95 % confidence level for any of the temperatures.

It was concluded that the material can be dispatched under ambient conditions without further precautions.

## 5.2   Long-term stability study

Data from the post-certification stability monitoring program for a SY124 in gas oil CRM, ERM-EF318, were available. A 144 month isochronous study was performed in this CRM. Units were stored at 18 °C for 0, 96, 120 and 144 months. The reference temperature was set to 4 °C. Two units per storage time were selected using a random stratified sampling scheme. From each unit, three samples were measured by HPLC-UV (Community Reference Method for the analysis of the Euromarker). The measurements were performed under repeatability conditions, in a random sequence to be able to separate any potential analytical drift from a trend over storage time.

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The long-term stability data for a storage temperature of 18 °C were evaluated. The results were screened for outliers using the single and double Grubbs test at a confidence level of 99 %. No outliers were found.

In addition, the data were plotted against storage time and linear regression lines of mass fraction versus time were calculated. The slopes of the regression lines were tested for statistical significance (loss/increase due to storage). No significant trend was detected for SY124 at a 95 % confidence level.

To verify that the data obtained from stability monitoring of similar CRMs produced and stored in the same way could be used to estimate the stability uncertainty contribution for ERM-EF318k, the data of the short term stability study were compared to the stability monitoring data. The data of the 60°C short-term stability study did not contradict the conclusions drawn from the long-term stability study on the uncertainty contribution relating to the storage of the CRM.

The results of the long-term stability measurements are shown in Annex C. The results of the statistical evaluation of the long-term stability study are summarised in Table 4.

**Table 4:** Results of the long-term stability tests

| Measurand | Number of individual outlying results* | Significance of the trend** |
|---|---|---|
| | 18 ºC | 18 ºC |
| SY124 | none | no |

  *  99 % confidence level

  ** 95 % confidence level

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.

## 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 repeatability, 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 [17] for SY124. 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:

$$u_{sts,rel} = \frac{s_{rel}}{\sqrt{\sum\left(t_i - \bar{t}\right)^2}} \cdot t_{tt}$$

**Equation 6**

$$u_{lts,rel} = \frac{s_{rel}}{\sqrt{\sum\left(t_i - \bar{t}\right)^2}} \cdot t_{sl}$$

**Equation 7**

$s_{rel}$      relative 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 60 ºC)

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

The following uncertainties were estimated:

- $u_{sts,rel}$, the uncertainty of degradation during dispatch. This was estimated from the 60 °C study. The uncertainty describes the possible change during a dispatch at 60 °C lasting for one week.

- $u_{lts,rel}$, the stability during storage. This uncertainty contribution was estimated from the 18 °C study.

The results of these evaluations are summarised in Table 5.

**Table 5:** Uncertainties of stability during dispatch and storage. $u_{sts,rel}$ was calculated for a temperature of 60 °C and 1 week; $u_{lts,rel}$ was calculated for a storage temperature of 18 °C and 24 months.

| Measurand | $u_{sts,rel}$ [%] | $u_{lts,rel}$ [%] |
|---|---|---|
| SY124 | 0.03 | 0.02 |

No significant degradation during dispatch even at 60 °C was observed. Therefore, the material can be transported at ambient conditions without special precautions.

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 value of a reference material.

This was based on a primary method of measurement confirmed by independent analyses. Gravimetric mixing was chosen as the method of choice. ERM-EF318k is a gas oil material

produced by gravimetrically mixing blank gas oil (free of SY124) and SY124 CRM certified for purity (ERM-AC316a). ERM-EF318k is certified for the SY124 mass fraction.

## 6.1    Purity of the base materials

The SY124 CRM certified for mass %, ERM-AC316a, was used to spike blank gas oil and the purity statement of the certificate of analysis was taken directly to calculate the certified value.

No indication was found that the blank gas oil used contained traces of SY124 (Section 3.12).

## 6.2    Mass fractions and their uncertainties

The certified mass values are based on the mass fractions of SY124 in gas oil, taking into account the purity of SY124. The values were calculated dividing the mass of the SY124 (in mg), corrected for its purity, by the final mass of the blank gas oil (in kg).

In Table 6, the data supporting the calculation of the mass fraction of SY124 is summarised.

**Table 6:** Subsequent mixing of SY124 (ERM-AC316a) with blank gas oil to prepare ERM-EF318k.

| | SY124 | | Gas oil | Mixtures |
| --- | --- | --- | --- | --- |
| | Mass [g] | Purity $\pm U\,(k=2)$ [%] | Mass [kg] | Calculated SY124 mass fraction [mg/kg] |
| Stock solution | 0.1286 | $95 \pm 1.2$ | 0.210 | 580 |
| ERM-EF318k | 0.1286[1] | $95 \pm 1.2$ | 14.044 | 8.70 |

[1] The whole stock solution was diluted by adding blank gas oil until the targeted mass was obtained.

The uncertainties of the certified mass fraction ($u_{char}$) of ERM-EF318k have several components i.e. the uncertainty of the mass determination of the stock solution and the uncertainties of the certified mass % of SY124.

The uncertainty of the gravimetric preparation of ERM-EF318k is summarised in Table 7.

**Table 7:** Uncertainty budget for the characterisation of SY124.

| | Value | $U$ | $k$ | $u_{rel}$ |
|---|---|---|---|---|
| **Purity SY124[1]** | 95 % | 1.2 % | 2.15 | 0.59 % |
| **Stock solution** | | | | |
| Mass SY124 | 0.1286 g | $8.04 \times 10^{-5}$ g | 2 | 0.03 % |
| Weighing boat | 0.4434 g | $8.13 \times 10^{-5}$ g | 2 | 0.01 % |
| **Final solution** | | | | |
| Mass gas oil (+stock solution) | 14.0442 kg | $2.88 \times 10^{-4}$ kg | 2 | 0.001 % |
| **Characterisation - ERM-EF318k[2]** | | | | |
| SY124/gas oil | 8.70 mg/kg | 0.10 mg/kg | 2 | 0.59 % |

[1] Data obtained from the certificate of analysis of ERM-AC316a.

[2] Relative standard uncertainty of the mass determination of gas oil for the preparation of ERM-EF318k, based primarily on the purity of the SY124 and the uncertainty of the weighing results. The whole stock solution was further diluted with gas oil to obtain the target mass fraction and for this reason the weighing of the gas oil in the stock solution was not taken into account to estimate the final uncertainty.

## 6.3   Verification measurements

Two units of ERM-EF318k and one unit of a quality control sample (ERM-EF318) were sent to two laboratories to be analysed in triplicate and in duplicate, respectively, by HPLC-UV (Community Reference Method). One of the laboratories reported two sets of data for each unit using the same analytical method but different instruments and they were treated as independent data sets (Annex D). Different units were analysed on different days but, due to the volatile nature of the matrix, measurements on each unit were performed under repeatability conditions.

The assessment of the verification measurements was performed by comparing the mean results of each unit with the certified value of ERM-EF318k following the procedure described in the ERM Application Note 1 [18]. The difference between the certified and measured values was compared with its uncertainty, i.e. the combined uncertainty of certified and measured value.

The difference between the mean measured value and the certified value, $\Delta_m$, can be calculated as:

$$\Delta_m = |c_m - c_{CRM}|$$    **Equation 8**

$c_m$          mean measured value

$c_{CRM}$          certified value

The uncertainty of $\Delta_m$ is calculated as:

$$U_\Delta = k.\sqrt{u_m^2 + u_{CRM}^2}$$

**Equation 9**

$U_\Delta$         combined uncertainty of result and certified value

$u_m$         uncertainty of the measurement result

$u_{CRM}$         uncertainty of the certified value

A coverage factor, $k$, of 2 corresponding to a confidence level of approximately 95 % was used.

If the absolute difference between the mean measured value and the certified value is equal or smaller than the expanded combined uncertainty of the measured value and certified value, $\Delta_m \leq U_\Delta$, then there is no significant difference between the measurement result and the certified value.

None of the unit means showed any significant difference from the certified value (Annex D).

# 7   Value Assignment

Certified and informative values were assigned.

<u>Certified values</u> are values that fulfil the highest standards of accuracy. Full uncertainty budgets in accordance with the 'Guide to the Expression of Uncertainty in Measurement' [6] were established.

<u>Additional material information</u> refers to values that were obtained in the course of the study. For example, results reported from only one or two laboratories or in cases where individual measurement uncertainty is high, would fall under this category.

## 7.1   Certified values and their uncertainties

The assigned uncertainty consists of uncertainties relating to characterisation, $u_{char}$ (Section 6.2), potential between-unit inhomogeneity, $u_{bb}$ (Section 4.1), and potential degradation during transport, $u_{sts}$, and long-term storage, $u_{lts}$ (Section 5). These different contributions were combined to estimate the relative expanded uncertainty of the certified value ($U_{CRM, rel}$) with a coverage factor $k$ given as:

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

**Equation 10**

-   $u_{char}$ 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 8.

**Table 8:** Certified values and their uncertainties for ERM-EF318k

| | Certified value [mg/kg] | $u_{char, rel}$ [%] | $u_{bb, rel}$ [%] | $u_{sts, rel}$ [%] | $u_{lts, rel}$ [%] | $U_{CRM, rel}$ [%] | $U_{CRM}$ [1] [mg/kg] |
|---|---|---|---|---|---|---|---|
| ERM-EF318k | 8.70 | 0.59 | 0.25 | 0.03 | 0.02 | 1.28 | 0.12 |

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

## 7.2    Additional material information

The data provided in this section should be regarded as informative only on the general composition of the material and cannot, in any case, be used as certified or indicative value.

The density of ERM-EF318k was determined in triplicate at 15 °C using ISO 12185:1996 method (Table 9).

**Table 9:** Additional material information for ERM-EF318k

| | Value [kg/m$^3$] |
|---|---|
| Density at 15 °C | 833.4 kg/m$^3$ |

This value corresponds to the unweighted mean value of two replicates performed in 3 independent 50 mL aliquots of the material. For each aliquot 13 units of ERM-EF318k were pooled.  ISO 12185:1996 [12] method was used to determine the density in the material at 15 °C by a single laboratory. The repeatability of the measurements according to ISO 12185:1996 is 0.2 kg/m$^3$ and the reproducibility is 0.5 kg/m$^3$. The additional material information value gives merely information about other material properties that may be of interest for the user.

# 8   Metrological traceability and commutability

## 8.1    Metrological traceability

**Identity**

SY124 is a chemically clearly defined analyte. Its identity was defined during the preparation and certification of ERM-AC316a [14]. The measurand is therefore structurally defined and independent of the measurement method.

**Quantity value**

The traceability chain is based on the use of calibrated balances, a thorough control of the weighing procedure and the purity of ERM-AC316a, which is traceable to the SI. The value in ERM-EF318k is therefore traceable to the SI unit of mass, kilogram.

## 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 [1] 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.

ERM-EF318k was produced by mixing a commercially available B0 gas oil and pure SY124, in order to be as similar as possible to the previous material, ERM-EF318. Since the production in 2005 of the first two SY124 in gas oil CRMs, ERM-EF317 and ERM-EF318, the commercially available gas oil in the European Union has been blended with biodiesel up to 7 % (v/v) [13] in order to reduce the emission of green-house gases [19]. Therefore, it is necessary to ensure that the analytical behaviour of ERM-EF318k, free of biodiesel, is the same as for routine gas oil samples.

To this end two commercially available gas oils (Table 10) were purchased and spiked gravimetrically with SY124 (ERM-AC316a) to obtain solutions at 125 %, 100 %, 50 % and 2 % of the marking level of ERM-EF318k. Aliquots of these solutions were analysed for SY124 content by two different methods, the Community Reference Method and DIN 51430 method.

**Table 10:** Characteristics of the two gas oils used in the commutability study.

| | FAME content, % (v/v)[1] | Density, kg/m$^3$ [2] |
|---|---|---|
| Gas oil 1 | 5.8 | 827.9 |
| Gas oil 2 | 6.5 | 828.8 |

[1] According EN 14078:2014, measurements carried out in duplicate

[2] According to ISO 12185:1996, measurements carried out in duplicate

The obtained results can be found in Annex E.

ERM-EF318k was produced by mixing gravimetrically commercially available B0 gas oil (without biodiesel) and SY124. As observed in the results (Annex E) the analytical behaviour of ERM-EF318k will be the same as for routine samples of commercial gas oil. For samples with higher biodiesel content than in B7 gas oil (biodiesel content of 7 %, v/v), the commutability has to be assessed.

# 9 Instructions for use

## 9.1 Safety information

The usual safety precautions for laboratory chemicals apply. The main hazard is the gas oil rather than the SY124.

The classification is according to Regulation (EC) No. 1272/2008 [39] and the usual hazard and precautionary phrases for gas oil diesel apply:

H226 - Flammable liquid and vapour.

H304 - May be fatal if swallowed and enters airways.

H332 - Harmful if inhaled

H373 - May cause damage to organs through prolonged or repeated exposure

H411 - Toxic to aquatic life with long lasting effects.

P261 - Avoid breathing dust/fume/gas/mist/vapours/spray

P280 - Wear protective gloves/protective clothing/eye protection/face protection.

P301+P310 - IF SWALLOWED: Immediately call a POISON CENTER.

P308+P313 - IF EXPOSED OR CONCERNED: Get medical advice/attention.

## 9.2 Storage conditions

The material can be stored at room temperature. Care should be taken to avoid exposure to light or other radiation.

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 ampoules.

## 9.3 Preparation and use of the material

The units shall be shaken by turning upside down for at least 2 min before opening to ensure material re-homogenisation

## 9.4 Minimum sample intake

The minimum sample intake is 20 µL.

## 9.5    Use of the certified value

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

Use as a calibrant

It is not recommended to use this matrix material as a calibrant. If used nevertheless, the uncertainty of the certified value shall be taken into account in the estimation of the measurement uncertainty.

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, www.erm-crm.org [2].

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 ($\Delta_{meas}$).

- 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 ($U_{\Delta}$) 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 material 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.

# 10 Acknowledgments

The authors would like to acknowledge the support received from J. Seghers from the JRC, Directorate F relating to the processing of this CRM and from F. Vanderveken concerning the set-up of the required isochronous studies.

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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: Results of the verification measurements**

**Annex E: Results of the commutability study**

# Annexes

**Annex A. Results of the homogeneity measurements**
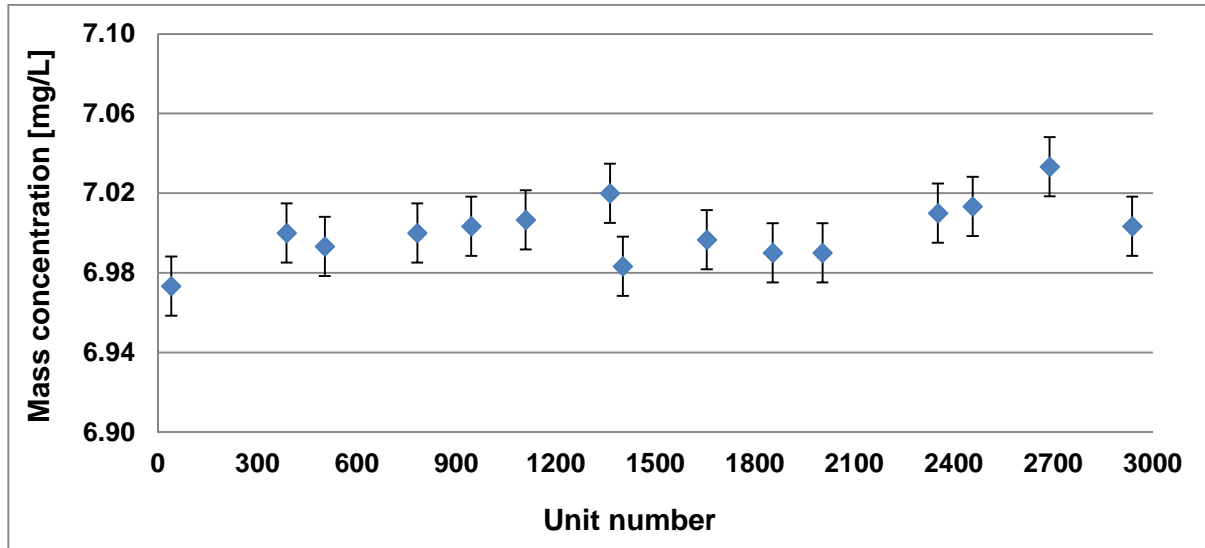


**Figure A.1.** Unit means for SY124 mass concentration, against unit number. Three replicates were analysed from each randomly selected unit (N = 15, n = 3). Vertical bars represent the 95 % confidence interval (CI) of the means.

**Annex B. Results of the short-term stability measurements**
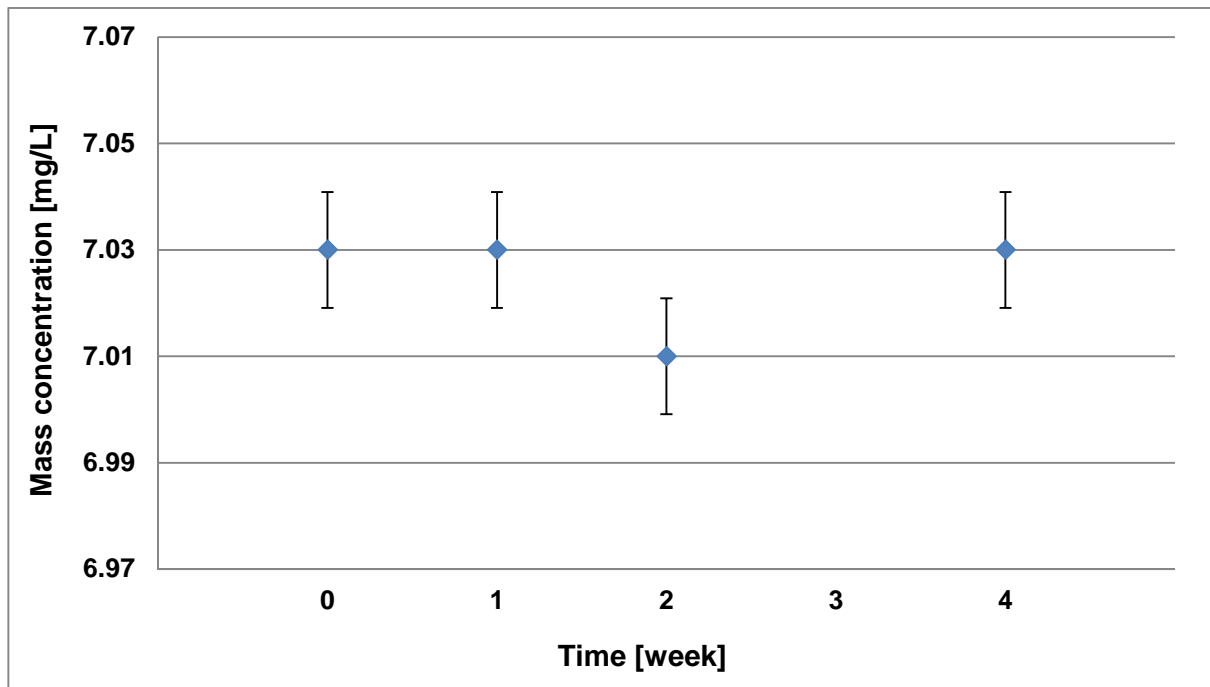


**Figure B1.** Data for the short-term stability study at 60 °C. The graph reports mass concentration means, obtained from the measurement of two units in duplicate per time point (N = 2, n = 2). Vertical bars represent the 95 % CI of the means.

## Annex C: Results of the long-term stability measurements
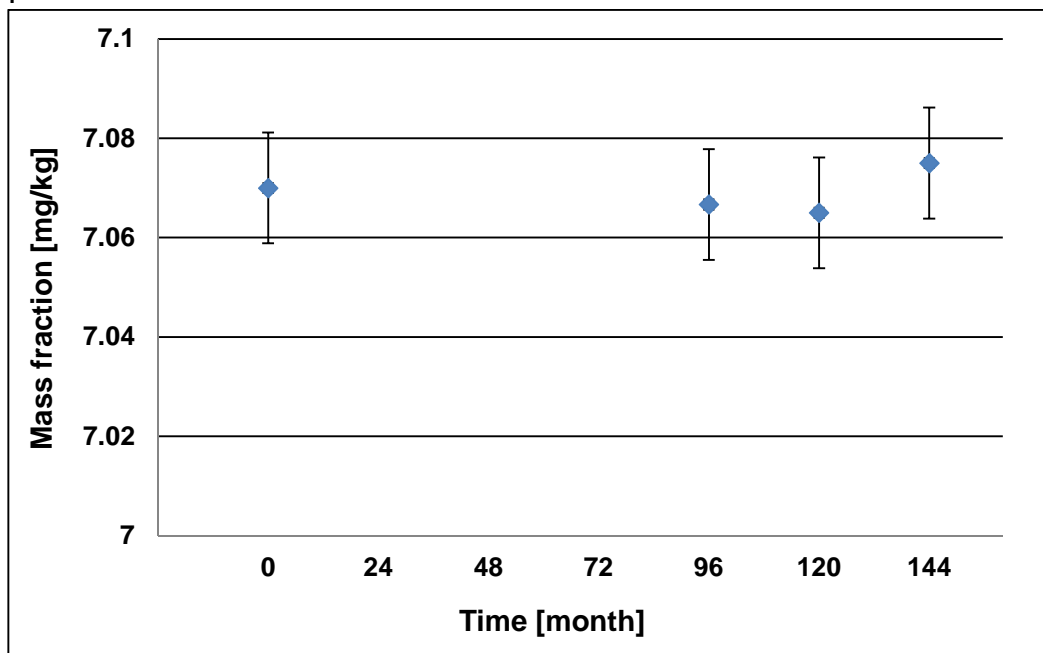


**Figure C1**. Data for the 144 months isochronous study during the post-certification stability monitoring of ERM-EF318 at 18 °C. The graph reports mass fraction means, obtained from the measurement of two units in triplicate per time point (N = 2, n = 3). Vertical bars represent the 95 % CI of the means.

**Annex D: Results of the verification measurements**
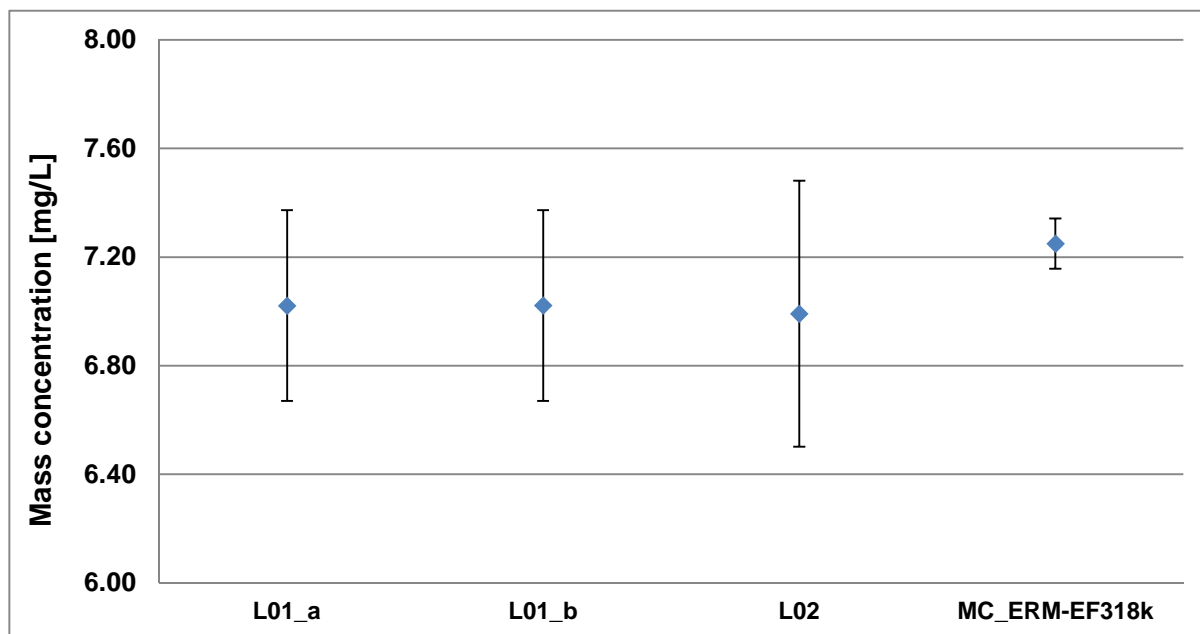


**Figure D1**. Results of the verification measurements performed in ERM-EF318k by two laboratories (L01 and L02) compared to the theoretical mass concentration of ERM-EF318k. The graph reports mass concentration means, obtained from the measurement of two units in triplicate per laboratory (N = 2, n = 3). The different sets for L01 (set a and b) were obtained by measurement of the samples in independent instruments. The sample MC_ERM-EF318k represents the certified mass fraction of ERM-EF318k converted to mass concentration units using the density of the material, 833.4 kg/m$^3$. Vertical bars represent the expanded uncertainty of the measurements ($k = 2$) and the theoretical expanded uncertainty of the ERM-EF318k mass concentration.

**Annex E. Results of the commutability study**

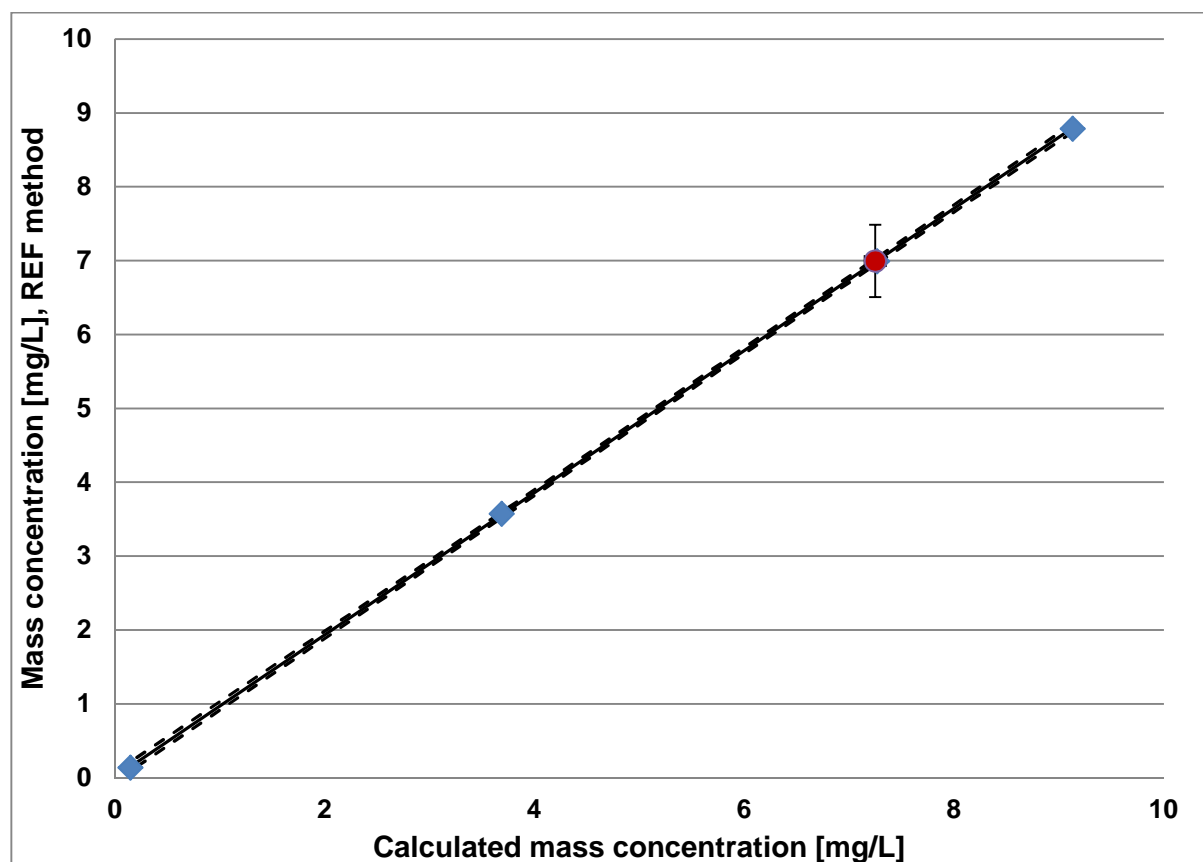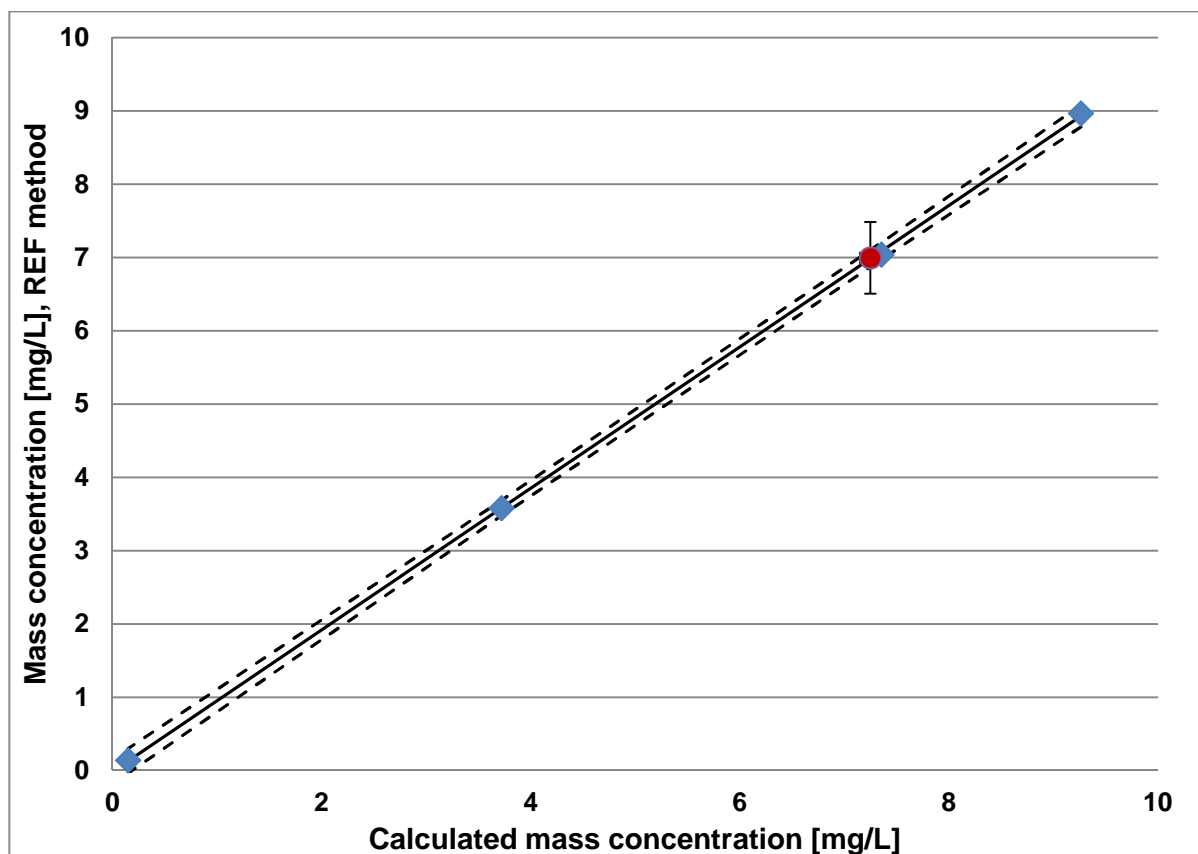**Comparison between different analytical methods**
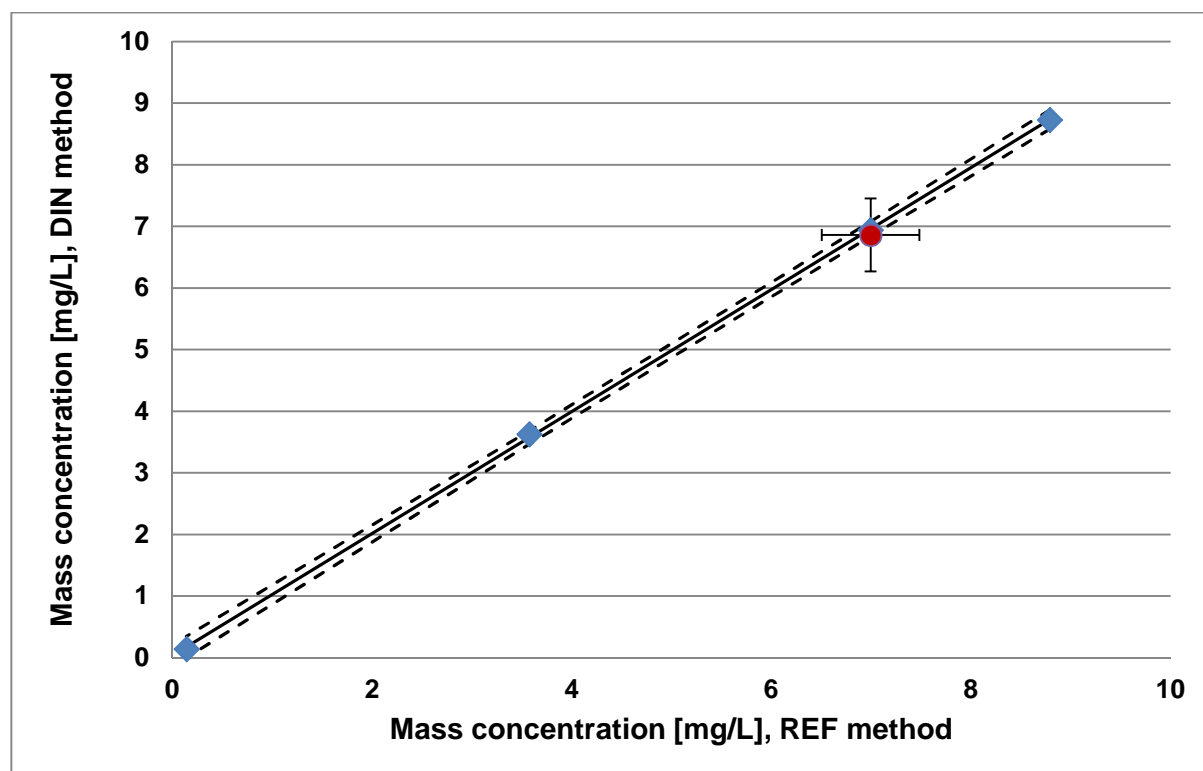


**Figure E1**. Data of commutability study for the samples prepared in gas oil 1 (diamond) and ERM-EF318k (round). The graph reports mass concentration means (N = 1, n = 2 per marking level and method) of the samples analysed by DIN 51430, DIN, and Community Reference Method, REF, for the analysis of SY124 in gas oil. The solid black line indicates the regression line of the gas oil 1 samples. The dotted lines show the 95 % CI of the regression line. Vertical and horizontal bars indicate the expanded uncertainty of the measurement results of ERM-EF318k.
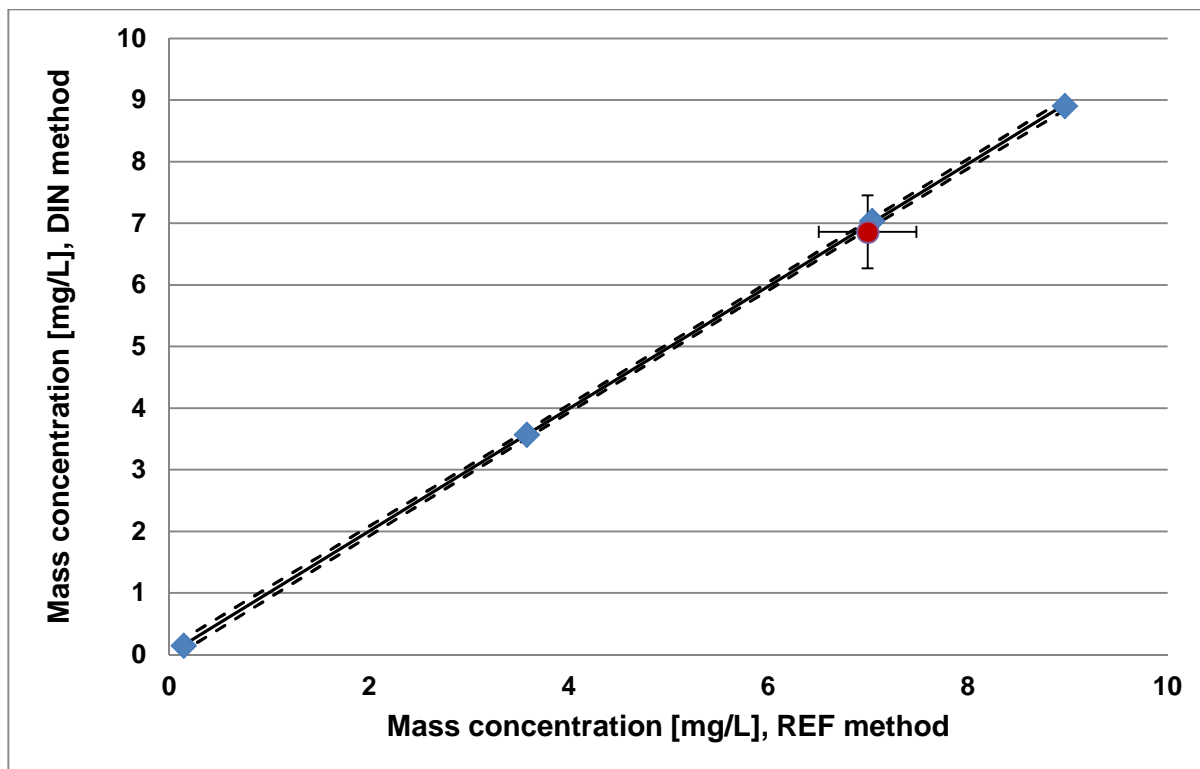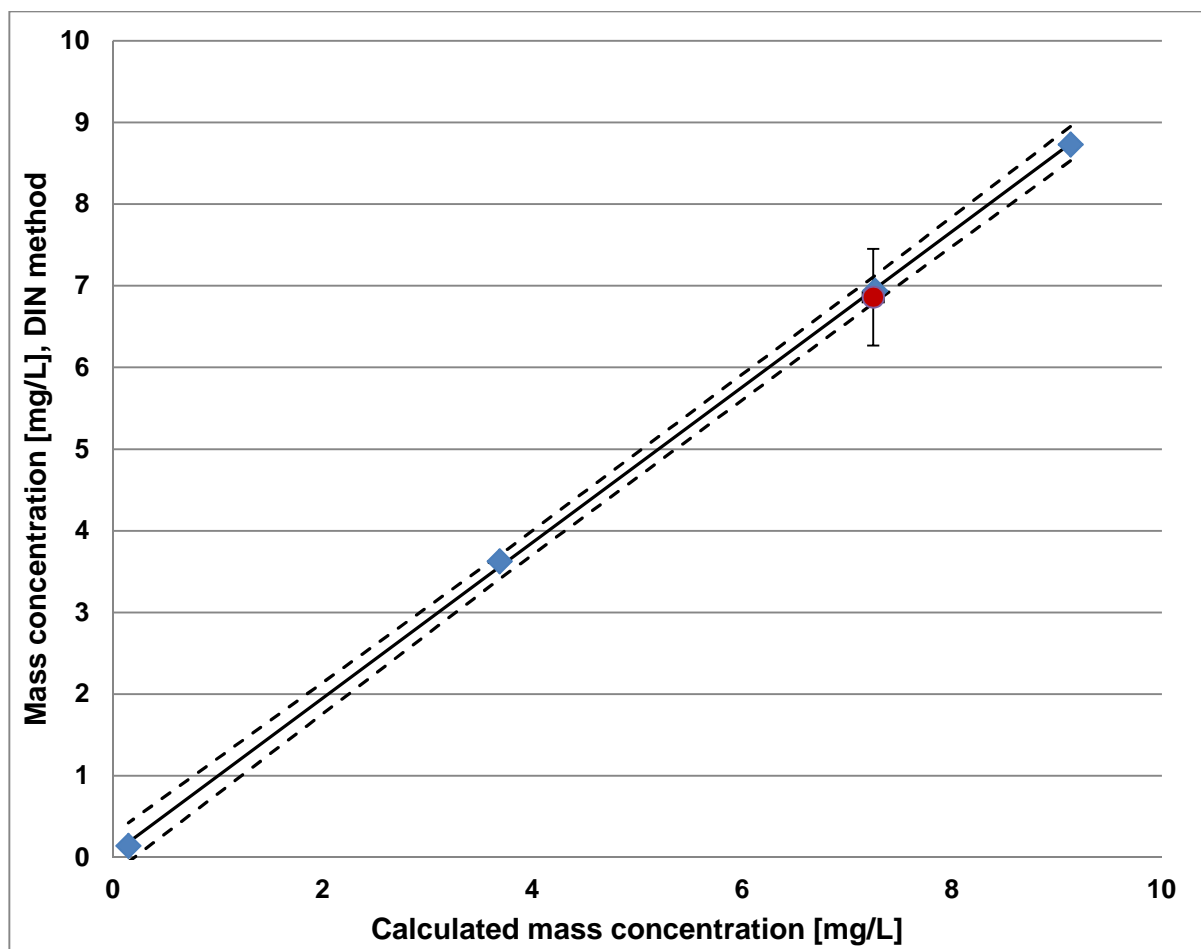
**Figure E2**. Data of commutability study for the samples prepared in gas oil 2 (diamond) and ERM-EF318k (round). The graph reports mass concentration means (N = 1, n = 2 per marking level and method) of the samples analysed by DIN 51430, DIN, and Community Reference Method, REF, for the analysis of SY124 in gas oil. The solid black line indicates the regression line of the gas oil 2 samples. The dotted lines show the 95 % CI of the regression line. Vertical and horizontal bars indicate the expanded uncertainty of the measurement results of ERM-EF318k.

**Comparison between the measured and calculated mass concentrations**



**Figure E3.** Data of commutability study for the samples prepared in gas oil 1 (diamond) and ERM-EF318k (round). The graph reports mass concentration means (N = 1, n = 2 per marking level) of the samples analysed by the Community Reference Method, REF, for the analysis of SY124 in gas oil and the mass concentration means calculated by gravimetric preparation. The solid black line indicates the regression line of the gas oil 1 samples. The dotted lines show the 95 % CI of the regression line. Vertical and horizontal bars indicate the expanded uncertainty of the measurement results of ERM-EF318k.
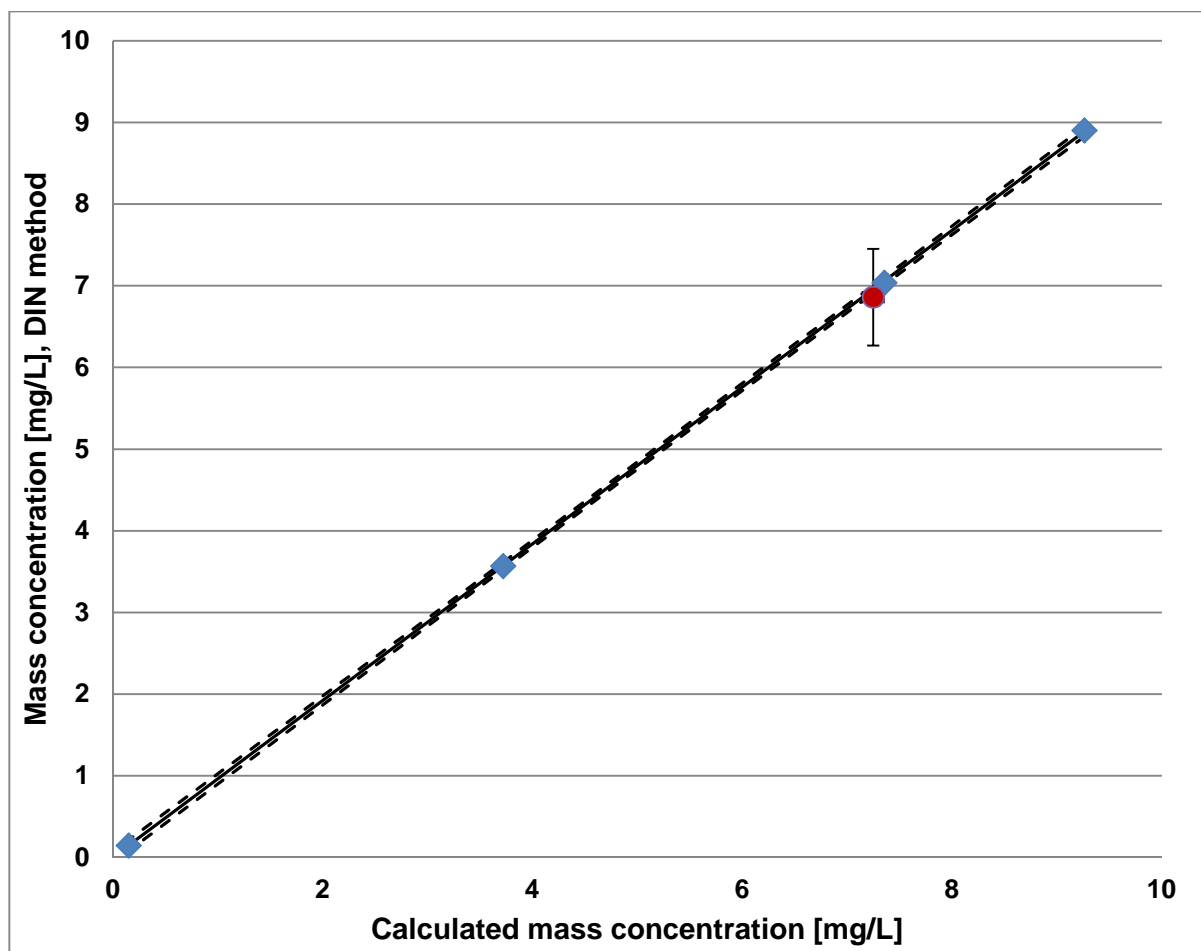
**Figure E4.** Data of commutability study for the samples prepared in gas oil 2 (diamond) and ERM-EF318k (round). The graph reports mass concentration means (N = 1, n = 2 per marking level) of the samples analysed by the Community Reference Method, REF, for the analysis of SY124 in gas oil and the mass concentration means calculated by gravimetric preparation. The solid black line indicates the regression line of the gas oil 2 samples. The dotted lines show the 95 % CI of the regression line. Vertical and horizontal bars indicate the expanded uncertainty of the measurement results of ERM-EF318k.

**Figure E5.** Data of commutability study for the samples prepared in gas oil 1 (diamond) and ERM-EF318k (round). The graph reports mass concentration means (N = 1, n = 2 per marking level) of the samples analysed by DIN 51430 Method, DIN, for the analysis of SY124 in gas oil and the mass concentration means calculated by gravimetric preparation. The solid black line indicates the regression line of the gas oil 1 samples. The dotted lines show the 95 % CI of the regression line. Vertical and horizontal bars indicate the expanded uncertainty of the measurement results of ERM-EF318k.

**Figure E6.** Data of commutability study for the samples prepared in gas oil 2 (diamond) and ERM-EF318k (round). The graph reports mass concentration means (N = 1, n = 2 per marking level) of the samples analysed by DIN 51430 Method, DIN, for the analysis of SY124 in gas oil and the mass concentration means calculated by gravimetric preparation. The solid black line indicates the regression line of the gas oil 2 samples. The dotted lines show the 95 % CI of the regression line. Vertical and horizontal bars indicate the expanded uncertainty of the measurement results of ERM-EF318k.

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