



# JRC REFERENCE MATERIALS REPORT

## Certification of the mass fraction and mass concentration of butoxybenzene in B7 gas oil: ERM-EF319

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## **Abstract**

ERM-EF319 is a B7 gas oil material, containing 7% of fatty acid methyl esters (B7 according to EN 590), certified for the mass fraction and mass concentration of butoxybenzene (butyl phenyl ether, CAS no. 1126-79-0), produced in accordance with ISO 17034:2016 [1] and ISO Guide 35:2017 [2].

The starting materials were commercially available B7 gas oil and butoxybenzene. The material was prepared gravimetrically using calibrated balances and the mass fraction was confirmed by independent measurements. The certified reference material (CRM) solution of butoxybenzene in B7 gas oil is available in glass ampoules containing at least 2.8 mL of the liquid material, which were sealed under an atmosphere of argon and stored at 18 °C in the dark.

Between-unit homogeneity was quantified and stability during transport and storage was assessed in accordance with ISO Guide 35:2017 [2]. Within-unit homogeneity was quantified to determine the minimum sample size. The minimum sample size for one measurement is 1 µL.

The certified value was obtained from the gravimetric preparations, taking into account the purity of the base materials. The certified values were confirmed by 2D-GC-MS.

Uncertainties of the certified values were calculated in accordance with ISO 17034:2016 [1] and ISO Guide 35:2017 [2] and include uncertainties related to possible inhomogeneity, instability and impurities.

The material is intended for the quality control and assessment of method performance.

Before release of the ERM-EF319, the certification project was subjected to peer-review involving internal and external experts.

## **Acknowledgements**

The authors would like to acknowledge the support received from colleagues of JRC for the processing, organising of stability studies, measuring, reviewing of the certification project and distribution of this CRM.

Furthermore, the authors would like to thank the experts of the Reference Material Review Panel Tuija Pihlström (Swedish Food Agency, SE) and Katrin Vorkamp (Aarhus University, DK) for their constructive comments and the external review of the certification report and certificate.

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# 1 Introduction

## 1.1. Background

In Europe, all gas oils and kerosene taxed at a rate different from the one used as propellant, i.e. road fuel, need to be marked with a fiscal marker (Council Directive 95/60/EC) [3]. This practice has the objective to counteract fraudulent use of energy products exempt from excise duty or subject to a reduced excise duty rate. To this end, a range of dyes have been used to facilitate the differentiation of the fuels with different prices in road side controls performed by many Member States of the European Union.

To aid the harmonisation of excise duties on mineral oils, the European Commission (EC) introduced Solvent Yellow 124 (SY124), N-ethyl-N-[2-(1-isobutoxyethoxy)ethyl]-4-(phenylazo)aniline (CAS number 34432-92-3) in 2002 as a common fiscal marker [4,5]. Following this decision, a method validation study was performed in March 2004 [6,7] and the community reference method was established. Two reference materials, ERM-EF318 and ERM-EF318k, containing SY124 at the marking level were produced for quality control by testing laboratories.

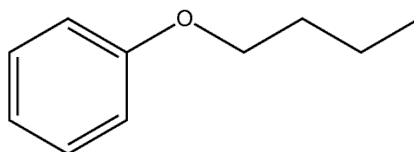
After technical developments in the field of marking systems and fraudulent activity notified by the Member States to the European Commission, revision of the Implementing Decision 2011/544/EU [8] became necessary by the end of 2016 to re-evaluate the suitability of SY124. Laundering of the Euromarker not only results in loss of income in the affected Member States but can also cause severe local environmental impacts due to the illegal dumping of toxic waste generated in SY124 removal activities.

As a consequence, in September 2015, the Directorate-General for Taxation and Customs Union, DG TAXUD, launched a Call for an Expression of Interest (CEI) to present new substances suitable for use as a marker in gas oils and kerosene (EU Official Journal No C299 of 11 September 2015). The CEI was structured to consist of two stages: First, the new substances were proposed by the applicants and evaluated based on documentary evidence (evaluation done by DG TAXUD, Directorate-General for Environment, DG ENV, and Directorate-General Joint Research Centre, DG JRC). Afterwards, four short-listed candidate markers should be thoroughly investigated alongside with SY124 by means of scientific laboratory experiments conducted by the JRC [9].

In January 2022, the European Commission published the Implementing Decision 2022/197/EU [10] electing ACCUTRACE™ PLUS containing butoxybenzene (CAS number 1126-79-0) as the preferred marker (Figure 1). Following the decision, ACCUTRACE™ PLUS should replace Solvent Yellow 124 as the common fiscal marker after an implementation transition period of 24 months, ending in January 2024. During this transition period, both markers are allowed to be used. The Member States set a marking level of at least 9.5 mg/L and not more than 14.25 mg/L of butoxybenzene. This decision is envisaged to be reviewed by the end of 2028 considering all technical developments in response to fraudulent use of fuels and tax evasion.

This report describes the production and certification of ERM-EF319, a CRM containing the new Euromarker, which will allow for calibration and quality control by testing laboratories.

**Figure 1.** Chemical structure of butoxybenzene.



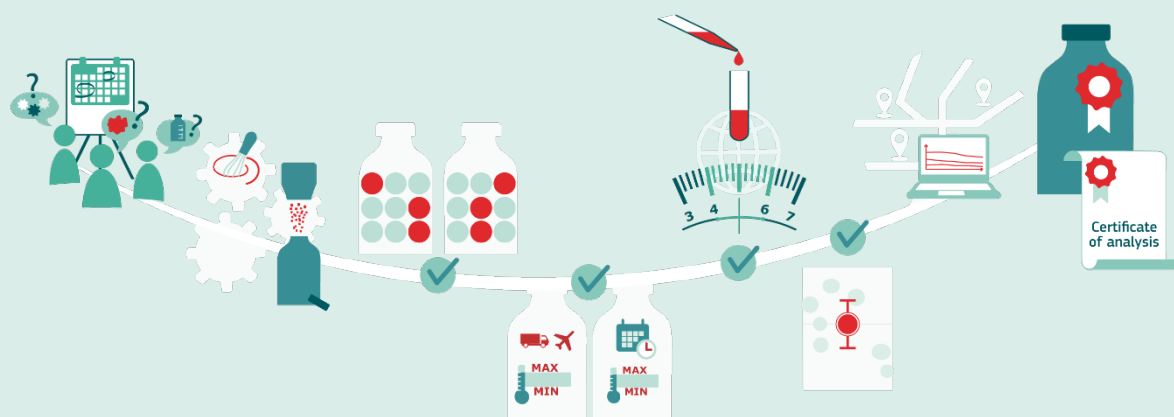
## 1.2. Choice of the material

ERM-EF319 is a B7 gas oil matrix containing the new Euromarker at the marking level and produced in support of the Commission Implementing Decision 2022/197/EU [10] under Directive 95/60/EC [3]. The previous certified reference material, ERM-EF318k, which had been developed in response to Commission Implementing Decision 2017/74/EU [11], can still be used in parallel with ERM-EF319 as long as SY124 would be used alongside with the new Euromarker.

ERM-EF319 was prepared using commercial B7 gas oil (according to EN 590), available at most fuel stations of the Member States. B7 gas oil is a winter diesel obtained from a randomly selected local fuel station. The commercially available butoxybenzene was purchased to prepare ERM-EF319 as it is the main substance of the new Euromarker elected by the European Commission. The mass fraction of butoxybenzene in ERM-EF319 complies with the marking interval of 9.5 mg/L and 14.25 mg/L established in Article 2 of the Commission Implementing decision 2022/197/EU [10].

## 1.3. Outline of the CRM project

### Box 1. Reference material production



Reference material (RM) production is defined in ISO 17034 [1] as a project comprising planning and processing of the material, followed by homogeneity and stability testing, characterisation and assigning of one or more property values. Depending on the intended use of the RM a commutability study is carried out.

For certified reference materials (CRMs) a certificate is issued while for RMs a product information sheet is issued by the reference material producer (RMP).

CRMs and RMs are distributed globally and the stability of their assigned values is monitored throughout the life-time of the material.

The selected starting materials and the preparation process followed the procedures used in the preparation of the previous Euromarker certified reference material, ERM-EF318k (SY124 in B0 gas oil).

ERM-EF319 was prepared from gravimetrically mixing the locally purchased B7 gas oil (according to EN 590) with butoxybenzene (CAS 1126-79-0). To ensure compliance with EN 590, additional characterisation of the B7 gas oil was performed. Two properties of the purchased B7 gas oil were verified: the density and the stated content of 7 % of fatty acid methyl esters (FAME).

The certified values for the mass fraction were obtained from the gravimetric preparation (weighing of the raw materials) of the solution, taking in consideration the purity of butoxybenzene which was determined at JRC-Geel. The methods used for the purity assessment were the mass balance approach (MB) and quantitative Nuclear Magnetic Resonance (qNMR). The density of ERM-EF319 was also determined using a primary method [2] to allow converting the certified value for the mass fraction (in mg/kg) into a certified mass concentration (in mg/L).



The certified values were confirmed by independent analyses in two laboratories using a two-dimensional gas chromatography-mass spectrometry (2D-GC-MS) method (ACCUTRACE™ PLUS method) [12]. The stability and homogeneity of the material were evaluated through dedicated studies.

Uncertainties of the certified values were estimated in compliance with ISO 17034 [1], which implements the basic principles of ISO/IEC Guide 98 (GUM) [13].

The CRM project, including the certification approach and the evaluation of the obtained measurement data, was subjected to peer-review involving both internal and external experts.

Certain commercial equipment, instruments, and materials are identified in this report to adequately specify 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.

## **2 Participants**

### **2.1 Project management and data evaluation**

European Commission, Joint Research Centre, Directorate F – Health and Food, Geel, BE

(accredited to ISO 17034:2016 for production of certified reference materials, BELAC No. 268-RM)

### **2.2 Processing**

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### **2.4 Stability measurements**

ALS Czech Republic, Prague, CZ

Dow Chemical Iberica S.L., Tarragona, ES

### **2.5 Characterisation measurements**

ALS Czech Republic, Prague, CZ

Dow Chemical Iberica S.L., Tarragona, ES

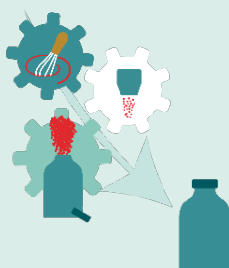
European Commission, Joint Research Centre, Directorate F – Health and Food, Geel, BE

IPQ Portugal, Lisbon, PT

All datasets are identified by a code (e.g. D01). The numbering is not related to the order of the laboratories presented above.

### 3 Material processing and processing control

#### Box 2. Reference material processing



RM processing covers the raw material conversion into a homogenous and stable material. It typically includes processing steps such as grinding or sieving and drying steps to enhance stability. When the processed material fulfils the specifications, the final material is filled into individual containers, referred to as RM units, such as bottles or ampoules and is labelled.

#### 3.1 Origin and Purity of the starting material

Butoxybenzene (buthyl phenyl ether, CAS 1126-79-0) is a commercially available substance purchased as a pure material from TCI Europe through VWR, Belgium. Identity was confirmed by  $^1\text{H-NMR}$  and GC-MS (Annex 4, Figures 4.2 and 4.3, respectively). The purity was determined at JRC-Geel using the averaged value obtained from the mass balance (MB) and qNMR methods. A detailed description can be found in section 6.

The matrix is B7 winter type gas oil compliant with EN 590 and purchased in January 2022 from a fuel station in Mol, BE. The material was tested for presence of butoxybenzene and no indication was found that the blank B7 gas oil matrix material contained traces of butoxybenzene above the limit of detection (LOD) of the 2D GC-MS method used (Section 6).

#### 3.2 Additional characterisation of the base materials

Prior to the processing of the ERM-EF319 material, the purchased B7 gas oil was further tested for compliance to EN 590 [14] for fatty acid methyl esters (FAME), density and water content. This standard establishes the requirements, test methods and threshold values for automotive gas oil in the EU and other European countries.

The FAME analysis was performed according to the EN 14078:2014 standard [15] to confirm the 7 % (volume fraction) of FAME present in the diesel. The analysis revealed a content of  $6.83 \pm 1.80$  % (volume fraction) of FAME in B7 gas oil.

The density of the pure B7 gas oil was confirmed for the temperature of 15 °C (reference temperature in petrol stations) using a stabinger viscometer to  $831 \text{ kg/m}^3$ , which complies with the density interval between 820 and  $845 \text{ kg/m}^3$  established in the EN 590 standard.

Water measurements on the B7 gas oil were carried out in duplicate by coulometric Karl-Fischer titration. The water content was under the 200 mg/kg limit.

The properties assessed proved that B7 gas oil is compliant with the EN 590 standard and can be used for preparing the CRM ERM-EF319.

#### 3.3 Processing

Until processing of the CRM material, both the B7 gas oil matrix and the butoxybenzene were stored at room temperature in the dark. The solution was prepared gravimetrically by addition of butoxybenzene to the B7 gas oil matrix.

The diesel was purchased from a local petrol station (Section 1.2) and combined into a single 20 L glass screw-cap bottle stirred for homogenization for 50 min with a magnetic stirrer. The tare of the 20 L glass bottle was measured five times using a Sartorius FCG 64 EDE-H balance prior to adding 2 L of B7 gas oil diesel.

In parallel, the mass of butoxybenzene to be spiked into the B7 gas oil was weighed using a Sartorius RC210S balance following a substitution weighing scheme, the ABBA weighing method [16]. In this procedure, an aluminium cap is weighed empty, the balance is tared and the empty cap is again weighed. Butoxybenzene is

carefully added to the aluminium cap using a gas-tight Hamilton syringe and the weight is recorded. The filled cap containing the butoxybenzene is dropped directly into the weighted 20 L glass bottle containing the 2 L of B7 gas oil. The remaining B7 gas oil is then poured into the weighed glass bottle. The averaged values of the weighings and the corresponding standard uncertainties are shown in Table 1.

**Table 1.** Averaged values and corresponding standard uncertainties obtained from the weighings of the raw materials.

Butoxybenzene mass $m \pm u_m$ [mg]	B7 Gas oil mass $m_{\text{gasoil}} \pm u_{m_{\text{gasoil}}}$ [kg]
211.9 $\pm$ 0.035	14.722 $\pm$ 0.001

The final solution containing the B7 gas oil, the butoxybenzene and the aluminium cap, is again weighed and stirred with a PTFE-coated magnetic bar for 18h prior to ampouling.

The ampouling was performed on a ROTA automatic ampouling machine, model R910/PA (ROTA Verpackungstechnik GmbH & Co.KG, Wehr, DE). The final solution is used to fill 2.8 mL of ERM-EF319 into 3 mL glass ampoules. These were flushed with argon prior to filling to remove most of the oxygen. The ampoules were flame-sealed directly after filling. The labelling of the ampoules was performed in fill-order so that each unit is associated with a unique identification number.

For the purpose of this report, the term ‘unit’ refers to one ampoule of ERM-EF319.

Six units of ERM-EF319 are shown in Figure 2.

**Figure 2.** Six units of the certified reference material ERM-EF319 containing the new Euromarker.



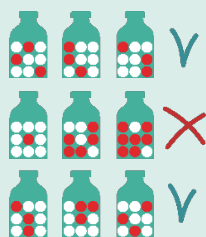
### 3.4 Processing control

After processing, six units were randomly selected and the water content was analysed using coulometric Karl-Fischer titration. The water content was below 200 mg/kg in all units tested. This quality criterion was predefined following the limits for water established in EN 590 [14].

The mass concentration of butoxybenzene in the B7 matrix was checked during homogeneity and short-term stability studies (Sections 4 and 5).

## 4 Homogeneity

### Box 3. Homogeneity assessment



A key requirement for any RM produced as a batch of units is equivalence between those units. It is important to know how much the variation between units contributes to the uncertainty of the certified value. Consequently, ISO 17034 [1] requires RMPs to quantify the between-unit variation in homogeneity studies.

The within-unit homogeneity is correlated to the minimum sample size, which is the minimum amount of sample that is, for a given measurand, representative of the whole unit and that should be used in an analysis. Using sample intakes equal to or above the minimum sample size guarantees the assigned value within its stated uncertainty.

The within-unit inhomogeneity does not influence the uncertainty of the certified value when the minimum sample size is respected, but determines the minimum size of sample that is representative for the whole unit. Quantification of within-unit homogeneity is therefore necessary to determine the minimum sample size.

### 4.1 Between-unit homogeneity

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

The number of units selected for determination of between-unit homogeneity corresponds to approximately the cube root of the total number of units produced. Accordingly, 18 units were selected using a random stratified sampling scheme covering the whole batch. Random stratified sampling involves dividing the batch into 18 groups (with a similar number of units in each group) and selecting one unit randomly from each group. Three independent samples were taken from each selected unit, and analysed by two-dimensional GC-MS (following the ACCUTRACE™ Plus Fuel Marker method). The measurements were performed under repeatability conditions and in a randomised manner to separate a potential drift in the measurement results from a potential trend in the filling sequence.

Regression analyses were performed to evaluate potential trends in the measurement sequence as well as trends in the filling sequence.

No trends in the filling sequence were observed at a 95 % confidence level. The individual results obtained for the butoxybenzene mass concentration against unit number (in filling order) is represented in a graphical form and is shown in Annex 1.

A significant trend in the measurement sequence was detected at a 95 % confidence level. During the measurements, the laboratory reported a recalibration in the middle of the sequence, which resulted in a marked shift of the results, creating two groups of results. This trend was corrected separately for each of the two groups.

Research has shown that the correction of even non-significant biases is beneficial. Such correction of non-significant biases has two advantages: Firstly, the resulting uncertainties are smaller than for non-corrected biases. Secondly, after correction the uncertainty interval has the highest probability of including the true value [17]. Correction of trends is therefore expected to improve the sensitivity of subsequent statistical analysis through a reduction in the variation of measurement results without masking potential between-unit heterogeneities. As the measurement sequence and the unit numbers were not correlated, trends significant on at least a 95 % confidence level were corrected as shown below:

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

$b$  slope of the linear regression  
 $i$  position of the result in the measurement sequence

The trend-corrected dataset was assessed for consistency using Grubbs outlier tests to the group average on the normalised data. One outlying individual result was detected at a 99 % confidence level and removed from the initial data set. This outlier corresponded to the first measurement of the second series. As the other two measurements from the same sample were in line with the other results and as the material is a true solution, this deviation was most likely caused by some startup effect and the result was therefore removed.

Quantification of between-unit inhomogeneity was evaluated by analysis of variance using a 2-way 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 a unimodal distribution and results for each unit that follow unimodal distributions 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 were available for the individual data making up the unit means to make a clear statement of the distribution. Therefore, it was checked visually whether all individual data followed 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.

It should be noted that  $s_{bb, \text{rel}}$  and  $s_{wb, \text{rel}}$  are estimates of the standard deviations and are therefore subject to random fluctuations. Therefore, the mean square between groups ( $MS_{\text{between}}$ ) can be smaller than the mean squares within groups ( $MS_{\text{within}}$ ), resulting in a negative number under the square root used for the estimation of the between-unit variation, whereas the true variation cannot be less than zero. As this is the case,  $u'_{bb}$ , the maximum inhomogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [18].  $u'_{bb}$  is comparable to the limit of detection (LOD) of a measurement method yielding the maximum degree of inhomogeneity that might be undetected by the given study setup.

Method repeatability ( $s_{wb, \text{rel}}$ ) (equivalent to the within-unit standard deviation) and  $u'_{bb, \text{rel}}$  were calculated as:

$$s_{wb, \text{rel}} = \frac{\sqrt{MS_{\text{within}}}}{\bar{y}} \quad \text{Equation 2}$$

$$u'_{bb, \text{rel}} = \frac{\frac{\sqrt{MS_{\text{within}}}}{n} \sqrt{4 \frac{2}{\nu_{MS_{\text{within}}}}}}{\bar{y}} \quad \text{Equation 3}$$

$MS_{\text{within}}$  mean of squares within-unit from ANOVA  
 $\bar{y}$  mean of all results of the homogeneity study  
 $n$  mean number of replicate analysis per unit  
 $\nu_{MS_{\text{within}}}$  degrees of freedom of  $MS_{\text{within}}$

When the homogeneity study shows no outlying unit means or trends in the filling sequence, the between-unit standard deviation is normally used as an estimate of  $u_{bb}$ . As  $MS_{\text{between}}$  is smaller than  $MS_{\text{within}}$ ,  $u_{bb}$  can't be estimated. As  $u'_{bb}$  sets the limits of the study to detect inhomogeneity,  $u'_{bb}$  is adopted as uncertainty contribution to account for the potential inhomogeneity.

The results of the evaluation of the between-unit variation are summarised in Table 2. The resulting value from the above equation was converted into a relative uncertainty ( $U_{bb,rel}^*$  and  $U_{bb,rel}$ ).

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

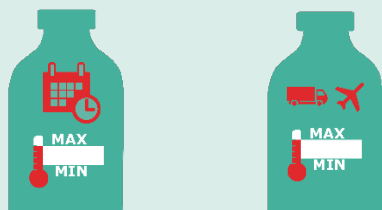
	$S_{wb,rel}$ [%]	$U_{bb,rel}^*$ [%]	$U_{bb,rel}$ [%]
Butoxybenzene	0.37	0.11	0.11

## 4.2 Within-unit homogeneity and minimum sample size

After mixing, the material is a true solution and is not expected to have any relevant inhomogeneity. This assumption was confirmed by the homogeneity study, where sample intakes as low as 1  $\mu\text{l}$  were found to give acceptable repeatability, demonstrating that there is no intrinsic inhomogeneity or contamination at a minimum sample intake of 1  $\mu\text{l}$ . The minimum sample size is therefore of 1  $\mu\text{l}$ .

## 5 Stability

### Box 4. Stability assessment



Stability testing is necessary to establish the conditions for storage as well as the transport conditions of the RMs to the customers. During transport, especially in summer, temperatures up to 60 °C can be reached, and stability under these conditions must be demonstrated if the RMs are to be transported without any additional cooling.

Time, temperature and light (including ultraviolet radiation) were regarded as the most relevant potential influences on the stability of the materials. The influence of ultraviolet and visible light is minimised by storing the material in amber containers, which reduce light exposure. In addition, materials are stored in the dark and transported in boxes, thus removing any possibility of degradation by light. Therefore, only the influences of time and temperature needed to be investigated.

The stability studies were carried out using an isochronous design [19]. In this approach, units were stored for a defined length of time under different temperature conditions. Afterwards, the units were moved to conditions where further degradation could be assumed negligible (reference conditions). At the end of the isochronous storage, the samples 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.

### 5.1 Transport stability

The conditions for the transport of the material to the customers were established in a short-term stability study. To this end, units were stored at 60 °C for 0, 1, 2 and 4 weeks. The reference temperature was set to 4 °C. Two units per storage time were selected for analysis using a random stratified sampling scheme. Of each unit, two samples were measured using the 2D GC-MS method. The measurements were performed under repeatability conditions, and a randomised sequence was used to differentiate any potential drift in the measurement results from a potential trend over storage time.

In addition, the data were evaluated against storage time, and regression lines of mass concentrations versus time were calculated, to test for potential increases or decreases of the butoxybenzene mass concentration due to shipping conditions. The slope of the regression line was tested for statistical significance.

A statistically significant trend in the measurement sequence was detected at a 95 % confidence level which was corrected following the procedure described in Section 4.1 and according to Equation 1 (Section 4). After correction, the data was re-evaluated and plotted against storage time. Although an apparent increase in the mean mass concentration for the last time point is visible, no significant trend was detected at a 95% confidence level from the linear regression applied to the mass concentration means versus time (Figure 2.1. in Annex 2).

In addition, the results were also screened for outliers using the single and double Grubbs test on a confidence level of 99 %. No outliers were detected and all data were retained for the estimation of the standard uncertainty of the short term stability,  $u_{\text{sts}}$  (Table 2).

Therefore, the material can be dispatched without further precautions under ambient conditions.

The results obtained from the storage stability study performed at 60 °C for the duration of one year (described in the following section) provide additional support to this conclusion.



## 5.2 Storage stability

Units were stored at 18 °C and 60 °C for 0, 4, 8 and 12 months (at each temperature). The reference temperature was set to 4 °C. Four units per storage time were selected using a random stratified sampling scheme. From each unit, two samples were measured using the 2D GC-MS method. The measurements were performed under repeatability conditions and in a random sequence to be able to separate any potential drift in the measurement results from a potential trend over storage time.

The long-term stability data were evaluated individually for each temperature. The results were screened for outliers using the single and double Grubbs test at a confidence level of 99 %.

In addition, the data were plotted against storage time and linear regression lines of mass concentration versus time were calculated. The slope of the regression line was tested for statistical significance (loss/increase due to storage).

No outliers or statistical trends were detected and all data were retained for the estimation of the standard uncertainty of the the long-term stability,  $u_{\text{ts}}$ . None of the trends was statistically significant on a 95 % confidence level for any of the temperatures. The material can therefore be stored at 18 °C.

The results of the long-term stability measurements are shown in Annex 3.

## 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 transport and storage were estimated for butoxybenzene in B7 gas oil, as described in [20]. In this approach, the uncertainty of the linear regression line with a slope of zero was calculated. The uncertainty contributions  $u_{\text{sts}}$  and  $u_{\text{ts}}$  were calculated as the product of the chosen transport time/shelf life and the uncertainty of the regression lines as:

$$u_{\text{sts, rel}} = \frac{s_{\text{rel}}}{\sqrt{\sum (t_i - \bar{t})^2}} \cdot t_{\text{tt}} \quad \text{Equation 4}$$

$$u_{\text{ts, rel}} = \frac{s_{\text{rel}}}{\sqrt{\sum (t_i - \bar{t})^2}} \cdot t_{\text{sl}} \quad \text{Equation 5}$$

$s_{\text{rel}}$	relative standard deviation of all results of the stability study
$t_i$	time elapsed at time point $i$
$\bar{t}$	mean of all $t_i$
$t_{\text{tt}}$	chosen transport time (1 week at 60 °C)
$t_{\text{sl}}$	chosen shelf life (12 months at 18 °C)

The following uncertainties were estimated:

- $u_{\text{sts,rel}}$ , the uncertainty of stability during transport. This was estimated from the 60 °C study. The uncertainty describes the possible change during a transport at 60 °C lasting for one week.
- $u_{\text{ts,rel}}$ , the uncertainty of stability during storage. This uncertainty contribution describes the possible degradation during storage for 12 months at 18 °C.

The results of these evaluations are summarised in Table 3.

**Table 3.** Uncertainties of stability during transport and storage.  $u_{sts,rel}$  was calculated for a temperature of 60 °C and 1 weeks;  $u_{lts,rel}$  was calculated for a storage temperature of 18 °C and 12 months.

	$u_{sts,rel}$ [%]	$u_{lts,rel}$ [%]
Butoxybenzene	0.03	0.59

In summary, no significant degradation at 18 °C and even at 60 °C was observed. Therefore, the material can be shipped at ambient conditions without special precautions and stored at 18 °C.

The material is included in JRC's regular stability monitoring programme, to check its further stability.

#### Box 5. Stability monitoring



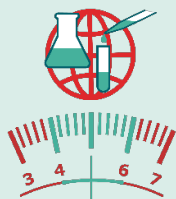
RMs are produced as batches that should last for ten years or longer. This long lifetime means that a storage stability study of limited duration cannot provide a definite “use by” date for the material. It therefore needs to be complemented by stability monitoring throughout the lifetime of the RM.

Therefore, the stability of RMs whose assigned values might change is regularly monitored. The monitoring frequency depends on the outcome of the storage stability assessment.

If the tests confirm the stability of the assigned values, the material remains on sale. If not, possible actions include the retraction of the value in question, retraction of the complete material or a change of the certified value. Customers are notified if the change is larger than the uncertainty of the assigned value.

## 6 Characterisation

### Box 6. Reference material characterisation



Material characterisation is the process of determining the property value(s) of a RM. While ISO 17034 [1] allows to characterise a RM in various ways. Quality management procedures of the JRC are more stringent and allow characterisation only by either interlaboratory comparison of expert laboratories or the use of a primary method confirmed by independent analysis.

For characterisation, gravimetry was chosen as primary method of measurement to assign the certified values for the mass fraction and mass concentration of butoxybenzene in B7 gas oil. The certified values were confirmed by an independent analysis via 2D-GC-MS.

ERM-EF319 is a B7 gas oil material produced by gravimetrically mixing blank B7 gas oil (according to EN 590) and butoxybenzene. The purity of the latter was determined to calculate the final certified values and the corresponding uncertainty ( $u_{\text{char}}$ ).

For the certification of the mass concentration, the density of ERM-EF319 was also measured using a primary method based on pycnometry according to the ISO 2811-1:2016 standard method [23]. The results obtained for the density were confirmed by additional density measurements obtained by an independent method using an oscillating U-tube densimeter (ISO 12185:1996) [21].

### 6.1 Purity of butoxybenzene

The purity of the butoxybenzene used for the processing of ERM-EF319 was investigated at JRC Geel to calculate the certified value for the mass fraction and the mass concentration of butoxybenzene. Two separate approaches were selected for a thorough evaluation of the purity of butoxybenzene: the indirect determination via the mass balance approach (MB) and the direct determination via quantitative NMR (qNMR) [22].

To quantify the mass fraction of the different classes of potential impurities (further referred as secondary components, SC), consisting of by-products, residual solvents or inorganic residues, three independent techniques were selected: thermogravimetric analysis coupled to gas chromatography and mass spectrometry (TGA-GC-MS), GC-MS and coulometric Karl-Fischer titration (C-KFT).

The details for the determination of the purity are described in Sections 6.1.1 and 6.1.2. All individual results grouped per method are displayed in Table 4 and in graphical form in Annex 4.

### 6.1.1 Mass balance approach

For the assessment of the purity of butoxybenzene using the MB method, the total mass fractions of the non-volatile ( $w_{NV}$ ) and organic volatile ( $w_{OV}$ ) impurities were quantified by TGA-GC-MS and the mass fraction of residual water ( $w_w$ ) by C-KFT. The mass fraction of the total related-structure impurities ( $w_{RS}$ ) was investigated by GC-MS.

The total mass fraction purity of butoxybenzene ( $w_{MB}$ ) is then obtained by subtracting the summed mass fraction impurities ( $w_I$ ) from the limit value for the mass fraction of butoxybenzene (1000 mg/g), as described in equation 6.

The combined standard uncertainty of  $w_{MB}$  is obtained from the combination of the standard uncertainties associated to each contributing impurity. Both equations for  $w_{MB}$  and  $u_{w_{MB}}$  are shown below:

$$w_{MB} = 1000 \text{ mg/g} - \sum w_I \text{ mg/g} \quad \text{Equation 6}$$

$$u_{w_{MB}} = \sqrt{\sum u_{w_I}^2} \quad \text{Equation 7}$$

#### 6.1.1.1 Mass fractions of the non-volatile ( $SC_{NV}$ ) and volatile ( $SC_V$ ) impurities

TGA-GC-MS was used for determining the mass fraction impurity for non-volatile ( $SC_{NV}$ ) and volatile ( $SC_V$ ) impurities. The mass fraction for the  $SC_{NV}$  impurities is given by weighing the residue remaining after exhaustive combustion at high temperature of the weighed butoxybenzene sample, whereas for the  $SC_V$  impurities, the sample is heated in a controlled manner at temperatures below the decomposition point and the total mass loss is equivalent to the mass fraction of the volatile material in the sample.

For these measurements, two independent ampoules previously filled with butoxybenzene were tested under intermediate precision conditions (1 ampoule on each day) to determine the mass fraction for each class of impurity tested (i.e. non-volatile and organic volatile impurities), with 3 replicates for each ampoule.

The absolute values obtained for the  $SC_{NV}$  and  $SC_V$  impurities were lower than the limit of detection (LOD) of the method (0.023 mg with an intermediate precision of 0.01 mg). Therefore, the mass fraction for both class of impurities ( $w_{NV/OV}$ ) is assigned to 0.0 mg/g.

As the mass fractions obtained for the two classes of impurities were too small to be quantitatively evaluated,  $w_{OV/NV}$  is assumed to be between zero and the LOD of the method,  $0 < w_{OV/NV} < \text{LOD}$ . As such, the standard uncertainties associated to the mass fraction estimation for the  $SC_{NV}$  and  $SC_V$  impurities were calculated following a rectangular distribution approach, using the mean value obtained from the minimum mass fraction detectable for butoxybenzene (relative LOD,  $\text{LOD}_{rel}$ ) and according to the equation shown below.

$$u_{w_{NV/NV}} = \frac{\bar{x}(\text{LOD}_{rel})}{\sqrt{3}} \quad \text{Equation 8}$$

The mass fractions of the  $SC_{NV}$  and  $SC_V$  impurities in butoxybenzene are estimated to  $0.0 \pm 0.57$  mg/g. Therefore, no  $SC_{NV}$  and  $SC_V$  impurities were detected with TGA-GC-MS. The uncertainty associated to the measurement is taken into account in the final uncertainty calculation of the MB approach as described in Equation 7 and in Section 6.1.1.4.

#### 6.1.1.2 Total related-structure impurities ( $SC_{RS}$ )

GC-MS was used to investigate the mass fraction of the  $SC_{RS}$  impurities ( $w_{RS}$ ) in butoxybenzene originating from contamination or butoxybenzene by-products possibly formed during the synthesis. A single analysis was performed on two different days. The total ion current chromatogram (TIC) of butoxybenzene is shown in Figure 4.3 in Annex 4. Butoxybenzene is the major peak identified in the TIC at retention time ( $t_R$ ) of 528

seconds, *s*. Phenol was also identified in the TIC as the largest impurity present ( $SC_{RS1}$ ) eluting at  $419 \pm t_R$ . Although other minor impurities were also detected, it was not possible to identify them. The mass spectrum of these impurities showed however, common fragment ions with butoxybenzene and the isomer *tert*-butoxybenzene (*t*-BPE).

To allow quantification of the mass fraction of the detected impurities ( $w_{RS}$ ), a calibration was performed for phenol and for *t*-BPE. Three solutions of butoxybenzene in diethyl ether were spiked with phenol and *t*-BPE at three mass fraction levels to derive the LOD.

Phenol ( $w_{RS1}$ ) was quantified with an impurity mass fraction of  $6.63 \pm 0.29$  mg/g.

For *t*-BPE and the other minor impurities ( $SC_{RS2}$ ), a conservative approach of estimation was used since they could not be identified but most contained common fragments with *t*-BPE. The relative signal of each impurity relative to the butoxybenzene signal was calculated for each measurement. The mean relative signals per impurity for all butoxybenzene measurements were summed. Applying the calibration function obtained for *t*-BPE, it resulted in an impurity mass fraction of  $2.26 \pm 0.08$  mg/g for the minor impurities ( $w_{RS2}$ ).

The estimation of the standard uncertainty of the measurement derived from the the repeatability and intermediate precision of the GC-MS method, where ANOVA was applied to the results obtained from 5 measurements performed in duplicate over 2 days.

The combined standard uncertainty is then calculated as

$$u_{w_{RS}} = \sqrt{u_{w_{RS1}}^2 + u_{w_{RS2}}^2} \quad \text{Equation 9}$$

The total mass fraction for the organic structure-related impurities corresponds to the sum of the mass fractions obtained for phenol and the minor impurities, estimated to 8.89 mg/g with a combined standard uncertainty of 0.30 mg/g.

#### 6.1.1.3 Water content ( $SC_w$ )

The C-KFT method was used to assess the mass fraction of the water content ( $w_w$ ) in two ampoules containing butoxybenzene. Samples were measured in triplicate and under intermediate precision conditions. The mass fraction of the water was estimated to 0.45 mg/g with a standard uncertainty of  $u_w = 0.05$  mg/g.

#### 6.1.1.4 Total purity of butoxybenzene ( $w_{MB}$ )

The total purity of butoxybenzene ( $w_{MB}$ , expressed as mass fraction), obtained via the mass balance method from the combination of all the  $SC_v$ ,  $SC_{NV}$ ,  $SC_{RS}$  and  $S_w$  impurities detected is then estimated to 990.7 mg/g with an expanded uncertainty of 1.7 mg/g ( $k = 2$ ) calculated from equations 6 and 7 described above. All individual results grouped per method are displayed in Table 4.

### 6.1.2 Direct assay by Quantitative NMR (qNMR)

Quantitative nuclear magnetic resonance (qNMR) is a direct method for purity determination of a target substance [22].

In this assay, the mass fraction purity of butoxybenzene ( $w_{qNMR}$ ) was determined following the internal standard method in which a defined amount of an internal standard is dissolved in a common appropriate solvent. The integral areas of the signal obtained for butoxybenzene were compared with the signal of the internal standard, *S*. The measurement equation from the approach used is given below (Eq. 10):

$$w_{qNMR} = R' \frac{N_S}{N_B} \frac{M_B}{M_S} \frac{m_S}{m_B} w_S \quad \text{Equation 10}$$

$R'$  is the average of all ratios  $\frac{I_B}{I_S}$  (the ratio of the integral of the butoxybenzene signal over the integral of the internal standard signal),  $N$  representing the number of  $^1\text{H}$  nuclei contributing to the integrated signals,  $M$  representing the molar mass,  $m$  representing the mass, and  $w$  representing the mass fraction purity. The indices B and S correspond to the analyte butoxybenzene and internal standard, respectively.

The internal reference standard used for the quantitative NMR measurements was dimethyl sulfone ( $\text{DMSO}_2$ , CAS No. 67-71-0) which is a certified reference material obtained from the Australian National Measurement Institute (NMIA, QNMR002) with a mass fraction purity ( $w_S$ ) of  $1000 \pm 0.8$  mg/g. The stated uncertainty is determined according to the ISO Guide 35 and representing the half width of a 95 % confidence range.

For the qNMR measurements executed at the JRC-GEEL, five ampoules containing the butoxybenzene and the internal standard  $\text{DMSO}_2$ , were prepared in duplicate, dissolved in deuterated chloroform ( $\text{CDCl}_3$ ) containing 0.03 % of tetramethylsilane (TMS) and measured under intermediate precision conditions.

The estimation of the standard uncertainty of the qNMR measurement was derived from the combination of the standard uncertainties for each term of equation 10, according to the measurement uncertainty and SI-traceability of direct methods described in the IUPAC Technical report [22].

The qNMR measurements lead to an averaged purity mass fraction ( $w_{\text{qNMR}}$ ) of 986.8 mg/g with an expanded uncertainty of 4.2 mg/g ( $k = 2$ ). The correspondent results are summarized in Table 4 and the  $^1\text{H}$ -NMR spectra of butoxybenzene is shown in Annex 4.

### 6.1.3 Assignment of the butoxybenzene purity value and uncertainties

Often, purity assessments undertake both direct and indirect determinations. Combining the results from multiple methods provides a result that is more likely to be accurate and provides greater confidence than a single estimate.

In this purity assessment, according to the procedure described in the ERM Application note 1 [30], the measured mean value and the uncertainties obtained from the two methods assessed (MB and qNMR), are not significantly different ( $\Delta m \leq \Delta U$ ). Therefore, the final butoxybenzene purity value ( $w_{\text{purity}}$ ) was estimated as a unweighted mean equal to 988.8 mg/g with a combined expanded uncertainty equal to 2.3 mg/g at a confidence interval of 95% ( $k=2$ ). The combined uncertainty was calculated according to the ISO/IEC Guide 98 (GUM) [13] as described in the equation below. The overview of the mass balance and qNMR results is shown below in Table 4 and in graphical form in Annex 4.

$$u_{\text{purity}} = \sqrt{\left(\frac{1}{2}\right)^2 u_{\text{MB}}^2 + \left(\frac{1}{2}\right)^2 u_{\text{qNMR}}^2} \quad \text{Equation 11}$$

**Table 4.** Summary of the averaged impurities determined by different methods following the mass balance approach and qNMR for the estimation of the total purity of butoxybenzene.

Butoxybenzene	Mean value [mg/g]	Standard uncertainty $u$ [mg/g]	Expanded uncertainty $U (k=2)$ [mg/g]
Inorganic Impurities			
TGA-GC-MS-NV	N.D. <sup>1)</sup>	0.57	1.14
TGA-GC-MS-V	N.D. <sup>1)</sup>	0.57	1.14
Organic impurities			
GC-MS	8.89	0.30	0.60
Water content			
C-KFT	0.45	0.05	0.10
Total MB and qNMR purity			
$w_{MB}$	990.7	0.86	1.7
$w_{qNMR}$	986.8	2.1	4.2
Final Purity			
$w_{purity}$	988.8 <sup>2)</sup>	1.1 <sup>3)</sup>	2.3

<sup>1)</sup> Not detected. The impurities are below method LOD (0.023 mg).

<sup>2)</sup> Calculated from the average of  $w_{MB}$  and  $w_{qNMR}$ .

<sup>3)</sup> Calculated combined uncertainty of MB and qNMR.

## 6.2 Density of ERM-EF319

To convert the certified mass fraction (mg/kg) to a certified mass concentration (mg/L), the density of ERM-EF319 was measured. To comply with the ISO Guide 35 for characterization measurements [2], a primary method (gravimetry) using the pycnometer method was chosen. The density measurements were performed at 20 °C as the verification analysis of the certified value were performed at room temperature via 2D-GC-MS (Section 6.4).

The laboratory performed the density measurements in triplicate and under intermediate precision conditions using 1 mL Gay-Lussac pycnometers according to the ISO 2811-1:2016 standard method [23]. Four independent units were randomly selected for each measurement. These were opened and combined in the same vial. Aliquots of 1 mL were taken to fill the pycnometer and perform the measurements. The reported expanded uncertainty is stated as the standard measurement uncertainty multiplied by the coverage factor  $k=2$ , which corresponds to a coverage probability of approximately 95 %. The uncertainty was calculated according to the Guide to the expression of uncertainty in measurement JCGM 100:2008 [24] and is in agreement with the ISO guide 35 for characterization measurements [2]. The uncertainty includes the individual quantification of the influence factors derived from the pycnometer method, including the reproducibility.

The density results and related uncertainty are given in Table 5.

**Table 5.** ERM-EF319 density averaged value and uncertainty obtained by a primary method (gravimetry).

ERM-EF319	Value [kg/m <sup>3</sup> ]	Standard uncertainty $u_{\text{density}}$ [kg/m <sup>3</sup> ]	Expanded uncertainty $U_{\text{density}} (k=2)$ [kg/m <sup>3</sup> ]
Density at 20.0 °C	822.0	2.7	5.4

### 6.3 Mass fractions and mass concentration and their uncertainties

The mass fraction certified value of ERM-EF319 is based on the weighings of the B7 gas oil and of the butoxybenzene (Table 1 in section 3.4), taking into account also the determined purity of butoxybenzene (Table 4 in section 6.1).

The certified mass concentration values are based on the certified mass fraction of butoxybenzene in B7 gas oil, which already takes into account the purity of butoxybenzene, plus the density, determined gravimetrically by the pycnometer method (Section 6.2).

The data supporting the calculation of the mass fraction and mass concentration of butoxybenzene are summarised in Table 6.

The uncertainties of the certified mass fraction of butoxybenzene ( $u_{\text{char, mf}}$ ) have several components i.e. the uncertainty of the mass determination of butoxybenzene ( $u_m$ ), the mass determination of B7 gas oil ( $u_{\text{m gasoil}}$ ) and the uncertainties of the purity determination of butoxybenzene ( $u_{\text{purity}}$ ). Based on the averaged value obtained from the mass balance and qNMR measurements, it was concluded that the purity of butoxybenzene is  $988.8 \pm 2.3$  mg/g (95 % confidence level,  $k = 2$ ). This value was taken into account when estimating the uncertainty of the certified value (Table 8).

**Table 6.** Relative uncertainty budgets for the characterisation of the mass fraction of butoxybenzene in ERM-EF319.

Butoxybenzene mass fraction [mg/kg]	Relative uncertainty contribution, [%]			Relative combined standard uncertainty $u_{\text{char, mf}}$ [%]
	$u_{m, \text{rel}}^{1)}$	$u_{m \text{ gasoil}, \text{rel}}^{2)}$	$u_{\text{purity}, \text{rel}}^{3)}$	
14.24	0.016	0.0048	0.11	0.12

<sup>1)</sup> Relative standard uncertainty of the weighed mass of butoxybenzene, based primarily on the uncertainty of the balance and the number of weighing steps required.

<sup>2)</sup> Relative standard uncertainty of the weighed mass of the gas oil based on the uncertainty of the balance and the number of weighing steps required.

<sup>3)</sup> Relative standard uncertainty of the purity estimation of the butoxybenzene, based on the uncertainty coming from the averaged values obtained from the mass balance and qNMR methods.



The uncertainties related to the certified mass concentration ( $u_{\text{char,mc}}$ ) of butoxybenzene (Table 7) comprise the uncertainty of the mass fraction (Table 6) and the uncertainty of the density measurements performed at 20 °C (Table 5).

**Table 7.** Uncertainty budgets for the characterisation of the mass concentration of butoxybenzene in ERM-EF319.

Butoxybenzene mass concentration [mg/L]		Relative uncertainty contribution, [%]				Relative combined standard uncertainty $u_{\text{char,mc}}^{5)}$ [%]
		$u_{m, \text{rel}}^{1)}$	$u_{m \text{ gasoil, rel}}^{2)}$	$u_{\text{purity, rel}}^{3)}$	$u_{\text{density, rel}}^{4)}$	
Butoxybenzene at 20.0 °C	11.70	0.016	0.0048	0.11	0.33	0.35

<sup>1)</sup> Relative standard uncertainty of the weighed mass of butoxybenzene, based on the uncertainty of the balance and the number of weighing steps required.

<sup>2)</sup> Relative standard uncertainty of the mass determination of B7 gas oil, based primarily on the uncertainty of the balance and the number of weighing steps required.

<sup>3)</sup> Relative standard uncertainty of the purity estimation of the butoxybenzene, based on the uncertainty coming from the averaged values obtained from the mass balance and qNMR methods.

<sup>4)</sup> Relative standard uncertainty of the density of butoxybenzene in B7 gas oil, based on the uncertainty of the primary method used (gravimetric).

<sup>5)</sup> Relative combined standard uncertainty of the mass concentration of butoxybenzene, based on the uncertainty from the mass fraction determination of butoxybenzene in B7 gas oil and the density measurements of the material at 20.0 °C performed by gravimetry.

## 6.4 Verification measurements

Two units of ERM-EF319 were sent to two laboratories to be analysed in triplicate using the same 2D-GC-MS method [12]. The different units were analysed on different days using an independent calibration standard (different supplier from the one used in the processing of the CRM). The reported data were treated as independent data sets (Annex 5.1).

The certified value of the mass concentration at 20 °C was confirmed by comparing the overall mean of the results ( $n=3$ ) obtained from each data set with the certified value of ERM-EF319 at 20 °C, following the procedure described in the ERM Application Note 1 [30]. The difference between the certified and measured values was compared with their uncertainty, i.e. the combined uncertainty of certified and measured value. The difference between the mean measured values and the certified value,  $\Delta m$ , can be calculated as indicated in Section 9.5. None of the means showed any significant difference from the certified value, which is therefore confirmed.

In addition, the correctness of the density measurements performed using a primary method, was also verified by an independent measurement method, following the requirements for characterization of a material in a single laboratory [2]. Twelve units covering the whole batch of ERM-EF319 were sent to a laboratory to be analysed using the oscillating U-tube method (ISO 12185:1996) [21] at the temperature of 20 °C. For each measurement, 3.5 mL of material is required so the contents of at least 2 units were pooled for each independent analysis. Each pooled amount was measured in triplicate and on two different days ( $N=6$ ,  $n=3$ ). The difference between the mean results of the two density measurements was compared with their combined uncertainty and showed no statistical difference. Therefore, the density value obtained by the primary method is confirmed.

The verification results are summarized in Annex 5.

## 7 Value Assignment

### Box 7. Assignment of values to a reference material



Based on the outcome of characterisation measurements three types of values can be assigned, namely certified, indicative or additional material information values.

Certified values are values that fulfil the highest standards of accuracy. Procedures at JRC Directorate F require a sufficient number of datasets to assign certified values. Full uncertainty budgets in accordance with ISO 17034 [1] and ISO Guide 35 [2] are required. Certified values of a CRM can be used for calibration and trueness controls.

Indicative values are values where either the uncertainty is deemed too large or too few independent datasets are available to allow certification. Indicative values of an RM can be used for statistical quality control (homogeneity and stability has been assessed) but not for calibration, demonstration of method or laboratory proficiency or method trueness.

Additional material information values are values for which homogeneity and stability has usually not been assessed and insufficient data for characterisation is available. Consequently, an estimate of the reliability of the values is not possible and no uncertainty is given. Additional material information values cannot be used for calibration, demonstration of method or laboratory proficiency or method trueness. They can be used to e.g. anticipate possible interferences in measurement processes.

Only certified values were assigned to this material. ERM-EF319 is certified for the butoxybenzene mass fraction (mg/kg) and for the mass concentration at 20 °C in B7 gas oil. The assigned values and correspondent uncertainty budgets for this material are summarized in Table 8.

### 7.1 Certified values and their uncertainties

The certified values assigned for the mass fraction are based on the weighings of butoxybenzene and gas oil used in the gravimetrical preparation and the purity of the butoxybenzene used as shown in section 6.1. For the mass concentration, the assigned values are based on the certified values of the mass fraction plus the density of the material as described in section 6.2.

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

$$U_{\text{CRM, rel}} = k \cdot \sqrt{u_{\text{bb, rel}}^2 + u_{\text{sts, rel}}^2 + u_{\text{lts, rel}}^2 + u_{\text{char, rel}}^2} \quad \text{Equation 12}$$

- $u_{\text{char}}$  was estimated as described in Section 6.2
- $u_{\text{bb}}$  was estimated as described in Section 4.1
- $u_{\text{sts}}$  and  $u_{\text{lts}}$  were estimated as described in Section 5.3

JRC's procedures for assigning uncertainties to certified values stipulate that a coverage ( $k$ ) factor of 2 can be chosen if the main uncertainty component has at least five degrees of freedom. As can be seen in Table 8, the  $u_{\text{lts, rel}}$  is the dominant contribution to the combined uncertainty and as it has 31 degrees of freedom for each temperature tested, a  $k$ -factor 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 its uncertainties for ERM-EF319.

	Certified value	$U_{\text{char, rel}}$ [%]	$U_{\text{bb, rel}}$ [%]	$U_{\text{sts, rel}}$ [%]	$U_{\text{lts, rel}}$ [%]	$U_{\text{CRM, rel}}$ [%]	$U_{\text{CRM}}^{1)}$ [mg/kg]
Butoxybenzene mass fraction [mg/kg]	14.24	0.12	0.11	0.03	0.59	1.22	0.18
Butoxybenzene mass concentration at 20 °C [mg/L]	11.70	0.35	0.11	0.03	0.59	1.39	0.17

<sup>1)</sup> Expanded ( $k = 2$ ) and rounded uncertainty; uncertainties are always rounded up [25] and in a way that the rounding error corresponds to 3 % to 30 % of the uncertainty.

## 8 Metrological traceability and commutability

### 8.1 Metrological traceability

#### Box 8. Metrological traceability

Metrological traceability of measurement results is a key requirement for ensuring the comparability of data. As CRMs are used to make measurement results traceable, metrological traceability of its certified values to a stated reference is essential.

The certified value of a CRM is metrologically traceable if the measurements used for establishing it can be related to a reference through an unbroken chain of calibrations.

This requires that these measurements

- refer to the same property (e.g. Pb) and the same (kind of) quantity (e.g. Pb content),
- result in a number and its uncertainty (e.g.  $6 \pm 2$ ) expressed in the same measurement unit (e.g.  $\mu\text{g/kg}$ ).

The concept of traceability rests on several anchor points, namely identity, quantity value and measurement unit. The identity of a measurand can be defined by its structure alone or can be operationally defined, the quantity value of the measurand can refer to the SI, or to other appropriate references.

#### 8.1.1 Identity

Butoxybenzene is a chemically clearly defined analyte. Identity was confirmed by  $^1\text{H-NMR}$  and GC-MS (Figures 4.2 and 4.3 in Annex 4) during the purity assessment prior the preparation of ERM-EF319. The measurand is therefore structurally defined.

#### 8.1.2 Quantity value

The traceability chain for the assigned values of butoxybenzene mass fraction is based on a calibration of the balances used that is traceable to the International System of Units (SI), plus a thorough control of the weighing procedure and the SI traceable purity value of butoxybenzene.

The traceability chain for the assigned values of butoxybenzene mass concentration is based on the SI-traceable calibration of the balances used for the weighings and the calibration of the pycnometer (primary method) used for density determination. In addition, the latter was also confirmed by an independent method of analysis. The density value is traceable to the SI.

The purity values have been obtained by a combination of the indirect mass balance approach (via the subtraction of the total SC impurities from unity) and with a direct quantification method, qNMR.

For the mass balance, the sum of the impurities as such is not a value traceable to SI, as it was not possible to identify and calibrate each measurement for the individual impurities. However, the purity of butoxybenzene is SI traceable, as the mass fraction contribution from all the SC impurities is small and associated with a conservative uncertainty estimate [22].

The values by qNMR are traceable to the SI by the traceability of the certified reference material used as internal standard for quantification.

The total purity values are therefore SI traceable.

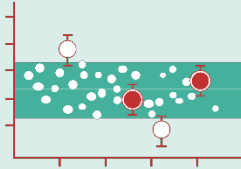
The values for mass fraction and mass concentration are therefore traceable to the SI.

## 8.2 Commutability

### Box 9. Commutability

Commutability is a prerequisite for RMs intended to be used for calibration or quality control of different measurement procedures targeting the same measurand. The concept of commutability of a RM is defined by the VIM [26] as:

*“property of a reference material, demonstrated by the closeness of agreement between the relation among the measurement results for a stated quantity in this material, obtained according to two given measurement procedures, and the relation obtained among the measurement results for other specified materials”*



Commutability is a property of an RM indicating how well an RM mimics the characteristics of a typical routine sample in various measurement procedures for a stated measurand.

The same RM may be commutable for some measurement procedures but non-commutable for others. A commutability statement is therefore only valid for the mentioned measurement procedure(s).

Commutability of this reference material does not need to be assessed as the matrix represents a real B7 gas oil sample.

## **9 Instructions for use**

### **9.1 Safety information**

The usual laboratory safety measures apply. The main hazard is the B7 gas oil.

The classification is according to Regulation (EC) No. 1272/2008 [27] and the usual hazard and precautionary phrases for gas oil apply:

Flammable liquids, Hazard Category 3

Aspiratory Toxicity, Hazard Category 4

Skin corrosion/irritation, Hazard Category 2

Acute Toxicity, Hazard Category 4

Carcinogenicity, Hazard Category 2

Specific Target Organ Toxicity – Repeated Exposure, Hazard Category 2

Hazardous to the aquatic environment – Chronic, Hazard Category 2

H226 Flammable liquid and vapour.

H304 May be fatal if swallowed and enters airways.

H315 Causes skin irritation.

H332 Harmful if inhaled.

H351 Suspected of causing cancer.

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

H411 Toxic to aquatic life with long-lasting effects.

P210 – Keep away from heat, hot surfaces, sparks, open flames, and other ignition sources. No smoking.

P260 – Avoid breathing dust/fume/gas/mist/vapours/spray

P273 – Avoid release to the environment

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

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

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

P331 – Do not induce vomiting.

P501 – Dispose of contents/container to an authorised waste collection point.

### **9.2 Storage conditions**

The material should be stored at room temperature in the dark. Care should be taken to avoid exposure to light or other radiation. The user should close any unit immediately after taking a sample, by transferring the remaining amount to another closed container.

For more information regarding the shelf life of reference materials please consult ERM Application Note 7 [28].

Note that the European Commission cannot be held responsible for changes that may happen to samples after opening or when the material is stored differently from the stated storage conditions at the customer's premises.

### **9.3 Use of the material**

For general information on handling of reference materials, please consult ERM Application Note 6 [29].

## 9.4 Minimum sample size

The minimum sample size representative for butoxybenzene in B7 gas oil is 1 µL.

## 9.5 Use of the certified value(s)

The intended use of this material is to assess method performance, i.e. for checking accuracy of measurement results. Using a CRM as quality control material in a measurement procedure serves to verify the metrological traceability. Certified values can be used for trueness controls.

### Use as a calibrant

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

### Comparing a measurement 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 [30]).

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 ( $\Delta_{\text{meas}}$ ).
- Combine the measurement uncertainty ( $u_{\text{meas}}$ ) with the uncertainty of the certified value ( $u_{\text{CRM}}$ ):  $u_{\Delta} = \sqrt{u_{\text{meas}}^2 + u_{\text{CRM}}^2}$
- 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  $\Delta_{\text{meas}} \leq U_{\Delta}$  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 Conclusions

ERM-EF319 is a matrix material certified for the mass fraction and mass concentration of butoxybenzene. This material was produced and certified in accordance with ISO 17034:2016 [1] and ISO Guide 35:2017 [2].

ERM-EF319 is produced in support of the revision of the Commission Implementing Decision 2022/197/EU [10] under the Directive 95/60/EC [3] to counteract fraudulent use of the previous Euromarker (Solvent Yellow 124) from laundering actions. The new Euromarker (ACCUTRACE™ Plus) is going to replace the current Euromarker (SY124, solvent yellow) from January 2024. The certified reference material ERM-EF319 will aid the control laboratories to assess their method performance, i.e. accuracy of measurement results.

The following values were assigned:

**Table 9.** Values assigned to ERM-EF319.

Certified values		
	Certified value <sup>1)</sup> [mg/kg]	Uncertainty <sup>3)</sup> [mg/kg]
Mass fraction of butoxybenzene	14.24	0.18
	Certified value <sup>2)</sup> [mg/L]	Uncertainty <sup>3)</sup> [mg/L]
Mass concentration of butoxybenzene at 20 °C	11.70	0.17
<sup>1)</sup> The certified value for the mass fraction is derived from the gravimetric preparation of butoxybenzene in B7 gas oil and from the purity assessment of butoxybenzene obtained from the averaged mass balance and qNMR methods. The certified values and their uncertainties are traceable to the International System of Units (SI). <sup>2)</sup> The certified values for the mass concentration are derived from the certified mass fraction and the density of the material, which was obtained by a primary method of measurement (gravimetry). The certified values and their uncertainties are traceable to the International System of Units (SI). <sup>3)</sup> The uncertainty of the certified value is the expanded uncertainty with a coverage factor $k = 2$ corresponding to a level of confidence of 95 %, estimated in accordance with ISO 17034:2016 and ISO Guide 35:2017		

The material is intended for the quality control and assessment of method performance.



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## List of abbreviations

ANOVA	Analysis of variance
$b$	Slope in the equation of linear regression $y = a + bx$
B7	Gas oil containing 7 % of FAME
BIPM	Bureau International des Poids et Mesures (International Bureau of Weights and Measures)
$c$	Mass concentration $c = m/V$ (mass/volume)
CEN	European Committee for Standardization
$CDCl_3$	Deuterated chloroform
CI	Confidence interval
C-KFT	Coulometric Karl Fischer titration
CRM	Certified reference material
EC	European Commission
EN	European norm (standard)
ERM <sup>®</sup>	Trademark owned by the European Commission; used by the JRC for reference materials
EU	European Union
FAME	Fatty acid methyl esters
GC-MS	Gas chromatography-mass spectrometry
GUM	Guide to the Expression of Uncertainty in Measurement (ISO Guide 98)
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
JRC	Joint Research Centre of the European Commission
$k$	Coverage factor
LOD	Limit of detection
LOQ	Limit of quantification
$\bar{m}$	Mean sample mass
$M$	Molar mass
MB	Mass Balance
MS	Mass spectrometry
$MS_{\text{between}}$	Mean of squares between-unit from an ANOVA
$MS_{\text{within}}$	Mean of squares within-unit from an ANOVA
$n$	Number of replicate analysis per unit
$N$	Number of units analysed
n.a.	Not applicable
qNMR	Quantitative Nuclear Magnetic Resonance
rel	Index denoting relative figures (uncertainties etc.)
RM	Reference material
$t_R$	Retention time

$s$	Standard deviation
$s_{bb}$	Between-unit standard deviation; an additional index "rel" is added when appropriate; this parameter is linked to the homogeneity of the material
$s_{between}$	Standard deviation between groups as obtained from ANOVA; an additional index "rel" is added as appropriate
SI	International System of Units
$s_{meas}$	Standard deviation of measurement data; an additional index "rel" is added as appropriate
$s_{wb}$	Within-unit standard deviation; this parameter is linked to the homogeneity of the material
$s_{within}$	Standard deviation within groups as obtained from ANOVA; an additional index "rel" is added as appropriate
SC	Secondary Component
$T$	Temperature
$t$	Time
TIC	Total ion chromatogram
TGA-GC-MS	Thermogravimetry analysis coupled to gas chromatography and mass spectrometry
$t_{sl}$	Proposed shelf life
$t_{tt}$	Proposed transport time
$u$	Standard uncertainty
$U$	Expanded uncertainty
$u'_{bb}$	Standard uncertainty related to a maximum between-unit inhomogeneity that could be hidden by 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
$w$	Mass fraction

$\bar{x}$	Arithmetic mean
$\bar{x}_{\max}$	Highest unit mean of the homogeneity study
$\bar{x}_{\min}$	Lowest unit mean of the homogeneity study
$\bar{x}_{\text{ns}}$	Arithmetic mean of all results of normal stock samples
$\bar{x}_{\text{ref}}$	Arithmetic mean of results of reference samples
$\alpha$	Significance level
$\Delta_{\text{meas}}$	Absolute difference between mean measured value and the certified value
$\nu_{s,\text{meas}}$	Degrees of freedom for the determination of the standard deviation $s_{\text{meas}}$
$\nu_{MS\text{within}}$	Degrees of freedom of $MS_{\text{within}}$
$\bar{y}$	Mean of all results of the homogeneity study

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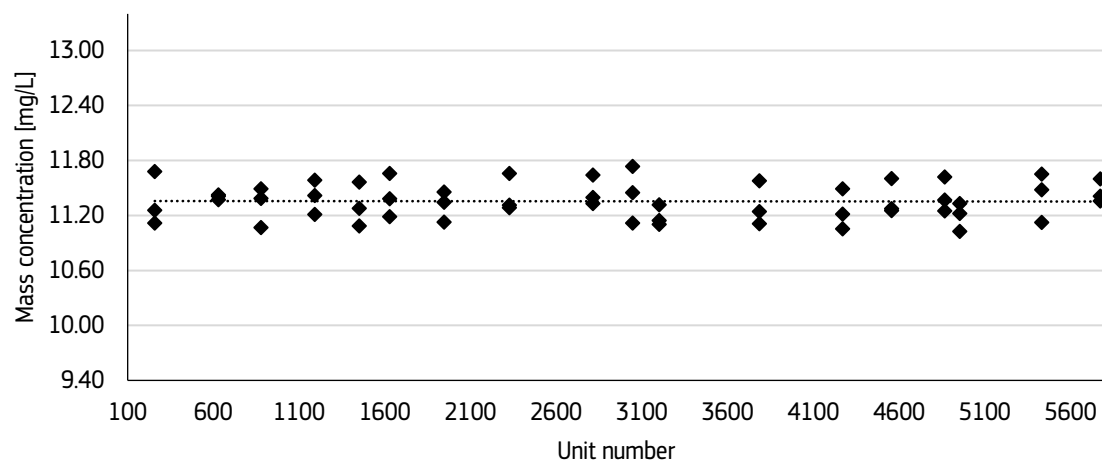
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## Annexes

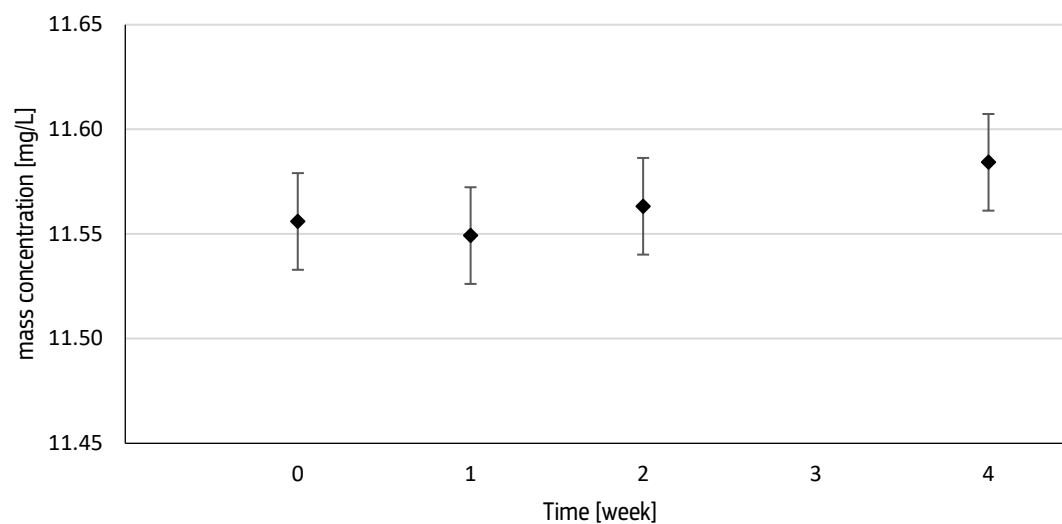
### Annex 1. Results of the homogeneity measurements

**Figure 1.1** Individual data points for the butoxybenzene mass concentration (before trend correction). Three replicates were analysed from each randomly selected unit ( $N = 18$ ,  $n = 3$ ).



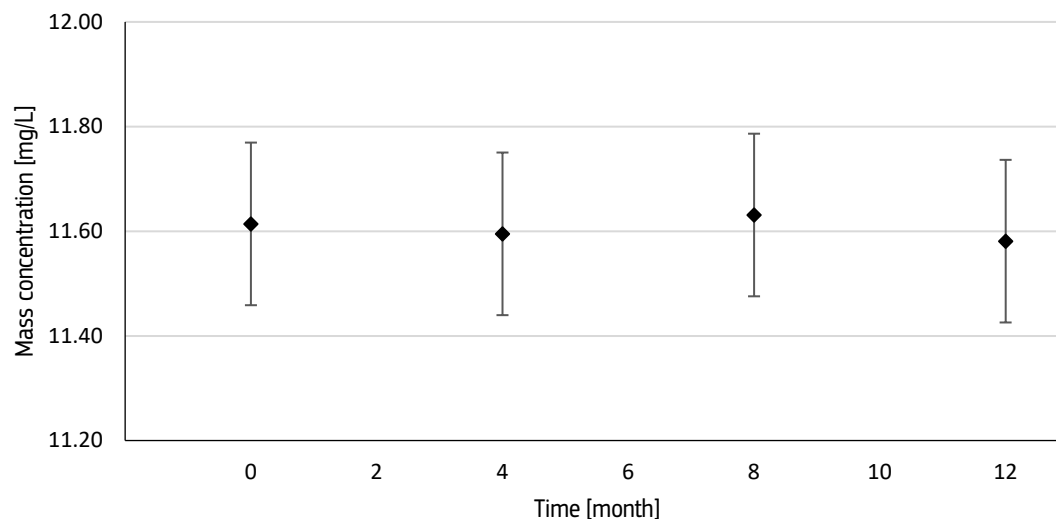
## Annex 2. Results of the transport stability measurements

**Figure 2.1** Transport stability of ERM-EF319 at 60 °C over four weeks. 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 mean per time point based on the within-group standard deviation ( $s_{wb}$ ) from ANOVA for all units.

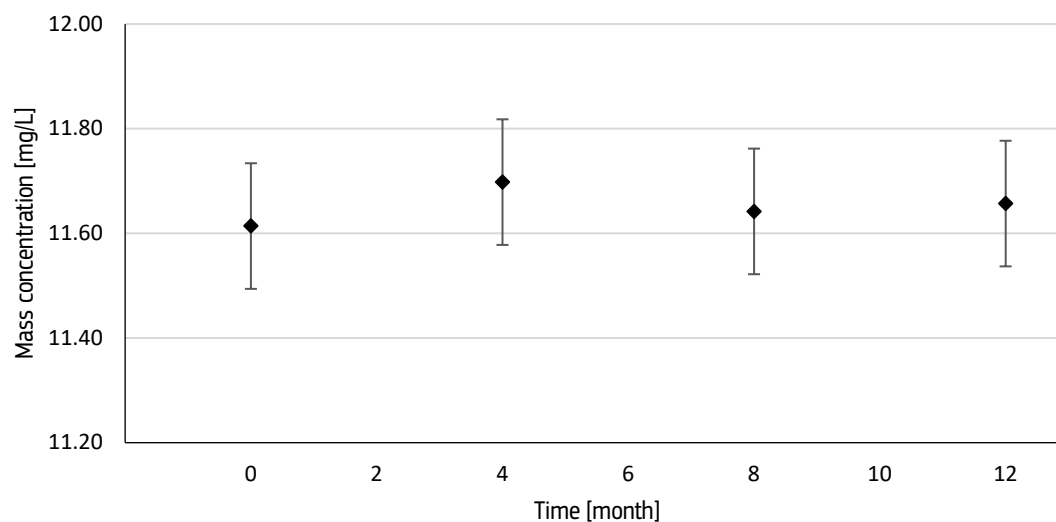


### Annex 3. Results of the storage stability measurements

**Figure 3.1.** Data for the 12 months isochronous study of ERM-EF319 at 18 °C. The zero time point corresponds to the reference temperature at 4 °C. The graph reports mass concentration means, obtained from the measurement of four units in duplicate per time point ( $N = 4$ ,  $n = 2$ ). Vertical bars represent the 95 % CI of the mean per time point.

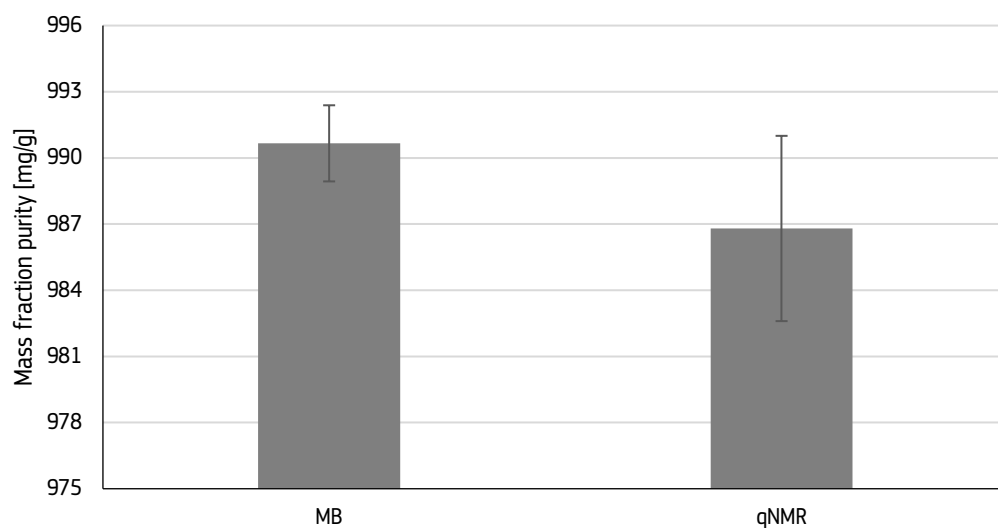


**Figure 3.2.** Data for the 12 months isochronous study of ERM-EF319 at 60 °C. The zero time point corresponds to the reference temperature at 4 °C. The graph reports mass concentration means, obtained from the measurement of four units in duplicate per time point ( $N = 4$ ,  $n = 2$ ). Vertical bars represent the 95 % CI of the mean per time point.

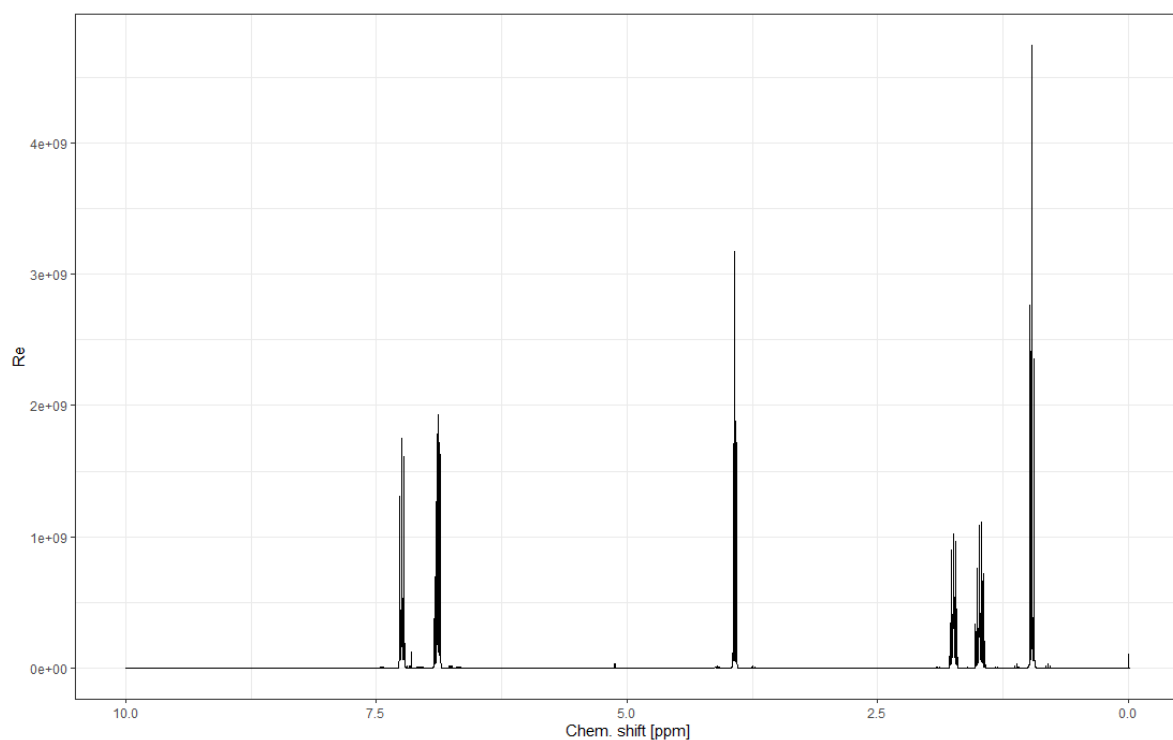


#### Annex 4. Summary of methods used in the characterisation study: Butoxybenzene purity assessment

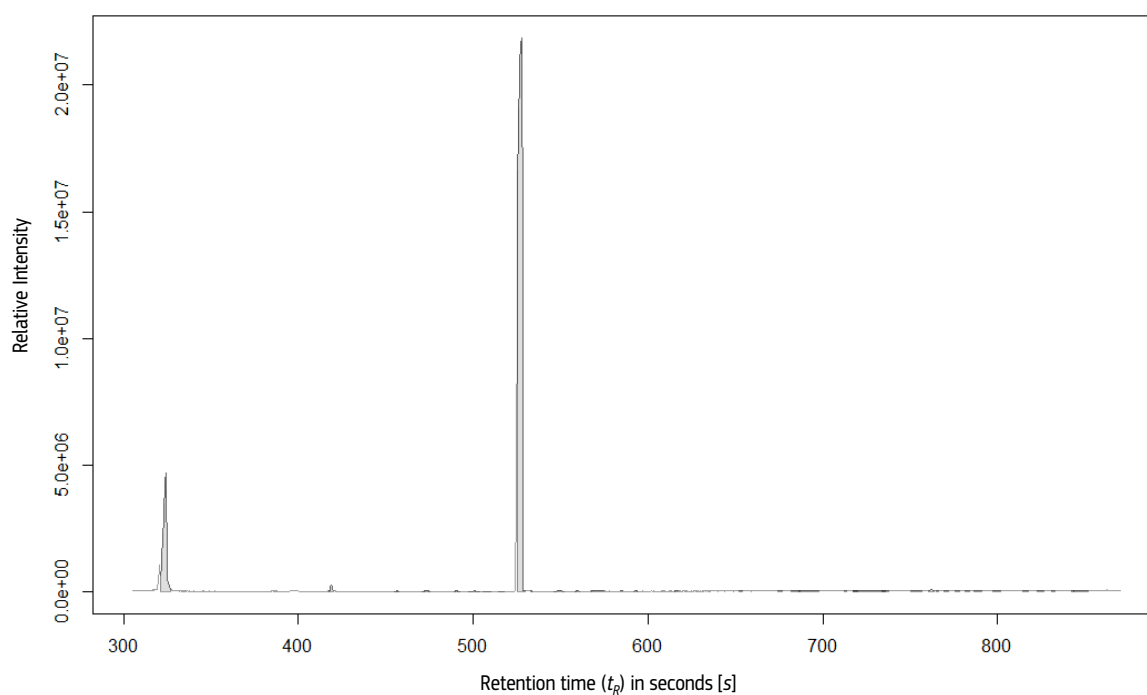
**Figure 4.1** Comparison of the results of the purity determination by mass balance (MB) and qNMR methods. The error bars represent the expanded uncertainty ( $k=2$ ).



**Figure 4.2**  $^1\text{H}$ -NMR spectrum of pure butoxybenzene in  $\text{CDCl}_3$ . The spectrum shows the relative intensity of each signal in arbitrary units against the chemical shift in ppm.



**Figure 4.3** Total ion chromatogram of butoxybenzene (528 s,  $t_R$ ) with phenol impurity visible at 419 s  $t_R$ . Peak at 320 s  $t_R$  corresponds to the solvent. The chromatogram shows the relative intensity of the peaks vs their retention time,  $t_R$ , in seconds (s).



## Annex 5. Results of the verification measurements

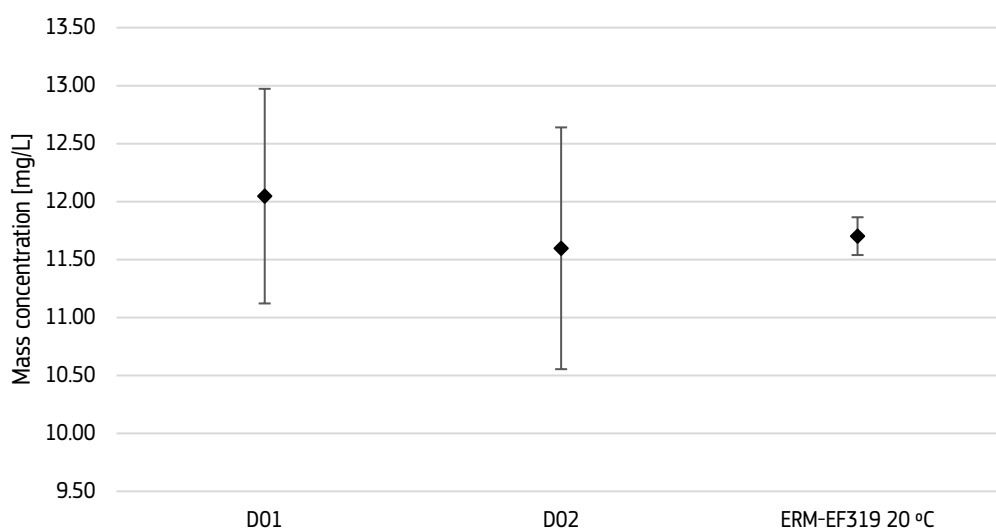
**Table 5.1** Results obtained from the verification measurements by 2D-GC/MS.

Dataset code and method	replicate 1 [mg/L]	replicate 2 [mg/L]	replicate 3 [mg/L]	replicate 4 [mg/L]	replicate 5 [mg/L]	replicate 6 [mg/L]	mean [mg/kg]	Expanded uncertainty [mg/L]
D01-2D-GC/MS	12.16	12.13	12.00	11.92	11.95	12.12	12.05	0.93
D02-2D-GC/MS	11.51	11.53	11.48	11.69	11.68	11.70	11.60	1.05

**Table 5.2** Results of the density measurements of ERM-EF319 at 20 °C by one laboratory using the pycnometer (D01) as a primary method (gravimetry) and the verification results obtained by measurements via the oscillating u-tube (D02).

Dataset code and method	replicate 1 [kg/m <sup>3</sup> ]	replicate 2 [kg/m <sup>3</sup> ]	replicate 3 [kg/m <sup>3</sup> ]	mean [kg/m <sup>3</sup> ]	Expanded uncertainty [kg/m <sup>3</sup> ]
D01-pycnometer 20 °C	820.60	823.30	822.00	821.97	5.40
D02- oscillating U-tube 20 °C	821.94	821.95	821.95	821.95	0.04

**Figure 5.1** Results of the verification measurements performed to ERM-EF319 by two laboratories (D01 and D02) compared to the mass concentration of ERM-EF319 at 20 °C. The graph reports mass concentration means, obtained from the measurement of two units in triplicate per laboratory ( $N = 2$ ,  $n = 3$ ). ERM-EF319 represents the certified mass fraction of ERM-EF319 converted to mass concentration units using the density of the material at 20 °C. Vertical bars represent the expanded uncertainty of the measurements ( $k = 2$ ) and the expanded uncertainty of the ERM-EF319 mass concentration at 20 °C.



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