



Certification Report

Certified Reference Material

BAM-K009a

**Lubricating oil
(additive free)**

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Summary

This report describes the preparation, characterization and certification of the reference material BAM-K009a. The certified reference material (CRM) is available as liquid diesel oil without solvents. BAM-K009a is intended to be used as calibration standard (type B) for the gas chromatographic determination of mineral oil hydrocarbons in water, soil and waste according to the analytical standard procedures ISO 9377-2, ISO 16703 and EN 14039.

The mass fraction of the boiling range between n-decane and n-tetracontane ($C_{10} - C_{40}$) has been certified for BAM-K009a:

Parameter	Value in g g⁻¹	Uncertainty U ¹⁾ in g g⁻¹
Mass fraction of the boiling range $C_{10} - C_{40}$	0.982	0.011

¹⁾ Estimated expanded uncertainty U with a coverage factor of $k = 2$, corresponding to a level of confidence of approximately 95 %, as defined in the Guide to the expression of uncertainty in measurement (ISO/IEC Guide 98-3:2008).

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List of abbreviations

(if not explained elsewhere)

ANOVA	Analysis of Variance
Bp	Boiling point
CRM	Certified reference material
FID	Flame ionization detector / detection
GC	Gas chromatography
IRH	Individual reference hydrocarbon
ISO	International Organization of Standardization
<i>k</i>	coverage factor
KFT	Karl-Fischer titration
MSDS	Material Safety Data Sheet
RHM	Reference hydrocarbon mixture
SOP	Standard operation procedure
TPH	Total petroleum hydrocarbons

1. Introduction

Mineral oils / mineral oil hydrocarbons (synonymously used term 'total petroleum hydrocarbons' TPH) are worldwide produced from crude oil and widely used for several kinds of products including fuels, motor-, heating- and lubricating oils. Large-scale handling, accidents and spills during production, transport and use lead to environmental contaminations, particularly related to water and soil compartments. Due to ecologically harmful and adverse health effects caused by TPH, the surveillance, determination and reduction of mineral oils in environmental matrices is subject to the work of legislative bodies, industry and chemical laboratories.

Reference materials and especially certified reference materials (CRM) are suitable tools to verify the accuracy of analytical measurements. Certified matrix CRMs for TPH determination in soil, sediment and waste are commercially available. The international standard methods for the determination of TPH in water, soil and waste (ISO 9377-2 [1], ISO 16703 [2] and EN 14039 [3]) are based on gas chromatography coupled to flame ionization detection (GC-FID). These standard methods define 'Mineral oil hydrocarbons/TPH' as non-polar substances (not adsorbing on Florisil® after extraction with non-polar solvents) in a boiling range between n-decane (C₁₀H₂₂) and n-tetracontane (C₄₀H₈₂). A mixture of equal amounts of two different oil types (type A/type B) is prescribed as calibration standard according to the standard methods stated above. Type A should show discrete peaks in the gas chromatogram, e.g. a diesel fuel without any additives. Type B should have a boiling range higher than that of type A and should have unresolved signals (hump) in the gas chromatogram, e.g. a lubricating oil [1,2,3]. Lot-no. I of BAM-K009 was produced and certified at BAM in 2000, which is sold out. This report describes the preparation, characterization and certification of lot-no. II of the BAM-K009 calibration standard indicated by the extension "a" (BAM-K009a). Certification of reference material BAM-K009a was carried out based on ISO 17034 [4] and the relevant ISO-Guides [5,6].

2. Preparation of BAM-K009a

2.1 Candidate Material

A lubricating oil (synonymously used terms: Lubricating base stock / lubricant), additive free paraffinic base oil, group II/II+ (Chevron Neutral Oil 100R) provided by Shell Global Solutions GmbH (Hamburg, Germany). It is a highly refined hydrogen treated crude oil distillate containing light and heavy paraffinic components. The density is 0.8505 kg/L (15°C) according to MSDS. The water content was determined by BAM to be 0.0027 % (coulometric KFT). The candidate material was bottled without any further treatment.

2.2 Bottling and storage

BAM-K009a was bottled in 3 mL amber glass vials sealed with crimp caps and PTFE inlets. 622 units of BAM-K009a were produced, each unit contains at least 2.0 mL (filled by using an automatic pipette, target volume: 2.1 mL). Each BAM-K009a

vial was additionally packed into a cardboard box with a foam insert. Besides general information, vials and cardboard boxes were undoubtedly labelled with specific vial-numbers. The whole batch is stored at room temperature at a dark place.

3. Mass fraction of boiling range decane (C₁₀) to tetracontane (C₄₀)

3.1 Principle and general remarks

The international standard methods for the determination of TPH in water, soil and waste (ISO 9377-2 [1], ISO 16703 [2] and EN 14039 [3]) are based on gas chromatography coupled to flame ionization detection (GC-FID). According to these standard methods, the TPHs are quantified in a defined boiling range between n-decane, C₁₀H₂₂ (C₁₀) and n-tetracontane, C₄₀H₈₂ (C₄₀). Therefore, the C₁₀-C₄₀ mass fraction is an important property value of BAM-K009a used as type B mineral oil calibration standard.

The determination of BAM-K009a's mass fraction of the boiling range between C₁₀ and C₄₀ is based on the BAM-internal SOP BAM-1.7-PV012 [7] describing the direct comparison of the FID-response of the mineral oil mixture with the FID-response of a reference hydrocarbon mixture (RHM). The RHM is consisting of several individual reference hydrocarbons (IRH) which should have the following properties:

- structurally/chemically defined hydrocarbons,
- different types of hydrocarbons (e.g., n-, cyclic- and branched aliphatic, mono-/di-cyclic aromatic compounds) which can also occur in natural mineral oils,
- high and known purities,
- boiling points within the range of C₁₀ to C₄₀,
- sufficient number of IRHs to simulate a representative mineral oil mixture.

The aim is to combine different IRHs resulting in a final mixture (RHM) that has similar properties as the natural mineral oil BAM-K009a. One of these similar properties is the carbon (C) content. This criterion results from the fact that the FID response is directly proportional to the C-content of a hydrocarbon. However, because the actual C-content of a real-world mineral oil mixture is always unknown, the RHM model with an average C-content can only be a best-praxis approach.

In addition to achieve comparable FID responses of BAM-K009a and RHM, gas chromatographic discrimination effects should be avoided. Therefore, measurements should always be performed with a non-discriminatory GC-FID system (e.g. on-column injection), also prescribed in [1,2,3].

To separate compounds according to their boiling points, non-polar GC columns are commonly used. According to the international standard procedures mentioned above, GC columns consisting of polydimethylsiloxane (95% to 100%) are typically used. To avoid systematic errors/shifts, GC-FID measurements to determine BAM-

K009a's mass fraction are performed on two non-polar GC columns with slightly different polarities. These (low bleeding) GC columns must be applicable up to high temperatures in order to analyse compounds until a boiling point of C₄₀ (525°C).

3.2 Reference hydrocarbon mixture (RHM)

Ten individual reference hydrocarbons (IRH), analytical standards with high purities supplied by Sigma-Aldrich, were selected for the preparation of the RHM based to the five criteria given above (3.1). Property values of the used IRH are summarised in Tab. 1.

Tab. 1: Individual reference hydrocarbons (IRH) for preparation of the reference hydrocarbon mixture (RHM)

IRH	Code	Sum formula	Bp (°C)	Provided purity (%)	Calculated Purity (%)	u_{pur} (%)
n-Pentylbenzene	PB	C ₁₁ H ₁₆	209.5	≥ 99.0	99.50	0.29
1,2,3,4-Tetrahydronaphthalene	THN	C ₁₀ H ₁₂	212.5	≥ 99.5	99.75	0.14
Tridecane	TD	C ₁₃ H ₂₈	234.0	≥ 99.5	99.75	0.14
Bicyclohexyl	BCH	C ₁₂ H ₂₂	239.7	≥ 99.0	99.50	0.29
Biphenyl	BP	C ₁₂ H ₁₀	254.8	≥ 99.5	99.75	0.14
2-Ethynaphthalene	EN	C ₁₂ H ₁₂	257.5	≥ 99.0	99.50	0.29
1-Phenyldodecane	PDD	C ₁₈ H ₃₀	331.0	≥ 99.5	99.75	0.14
1-Phenyltetradecane	PTD	C ₂₀ H ₃₄	357.3	≥ 99.5	99.75	0.14
Docosane	DC	C ₂₂ H ₄₆	369.0	≥ 99.5	99.75	0.14
Squalane	SQA	C ₃₀ H ₆₂	416.5	97.20 ^a	97.20	0.25 ^b

^a) The 'provided purity' of squalane (97.2 %) is a certified value of the supplier and set to 'calculated purity'

^b) The uncertainty of squalane's purity (0.25 %) was taken from supplier's certificate.

Tab. 1 displays the calculated purities (pur_{cal}) of the IRH determined using Eq. 1 based on a rectangular distribution. The pur_{cal} values were used to determine the concentration of the RHM solution (Tab. 2).

$$pur_{cal} = pur_{pro} + \left(\frac{100 - pur_{pro}}{2} \right) = pur_{pro} + HW_{rec} \quad \text{Eq. 1}$$

pur_{cal} calculated purity (%)
 pur_{pro} provided purity (%) by the suppliers
 HW_{rec} half width of the rectangular distribution

The corresponding uncertainty of the 'calculated purity' (u_{pur}) was determined using Eq. 2 based on the uncertainty calculation of a rectangular distribution:

$$u_{pur} = \frac{HW_{rec}}{\sqrt{3}} \quad \text{Eq. 2}$$

At first, separate solutions of the IRHs were gravimetrically prepared in n-heptane with concentrations of about 4.4 mg/g for each compound considering the purity (pur_{cal}) of each IRH according to Tab. 1. Before further mixing, the purities of the

IRH provided by the suppliers (Tab. 1) were checked by GC-FID (BPX-5 column). Because these control measurements confirmed supplier's purities, the IRHs were taken for subsequent processing. Equal volumes of each IRH solution (10 mL) were combined in a 100 mL flask (Tab. 2) - all steps were gravimetrically controlled.

Tab. 2: Preparation of the reference hydrocarbon mixture (RHM) from 10 IRH solutions

Individual reference hydrocarbon (IRH)	IRH solution ^a (g)	IRH absolute ^a (mg)	Uncertainty IRH ^a (mg)	Conc. IRH ^b (mg/g)	Uncertainty IRH ^b (mg/g)
PB	6.8181	30.8097	0.0889	0.4518	0.0013
THN	6.8145	30.3984	0.0439	0.4458	0.0006
TD	6.8129	30.2574	0.0437	0.4437	0.0006
BCH	6.8182	30.2660	0.0874	0.4439	0.0013
BP	6.8292	29.8941	0.0431	0.4384	0.0006
EN	6.8217	30.3611	0.0876	0.4452	0.0013
PDD	6.8105	30.0166	0.0433	0.4402	0.0006
PTD	6.8340	30.1202	0.0435	0.4417	0.0006
DC	6.8105	30.2764	0.0437	0.4440	0.0006
SQA	6.8198	29.1378	0.0728	0.4273	0.0011
Total (RHM):	68.1894	301.5377	0.1998	4.4221	0.0088 ^c

^a) Mass of IRH-solution (g) 1st col., abs. IRH mass (mg) 2nd col. and its uncertainty (mg) 3rd column

^b) IRH concentration in the final RHM-solution (4th column) and its uncertainty (5th column)

^c) Sum of 10 IRH uncert. as worst-case estimation (compared to 0.0029 mg/g as root of sum squares)

The concentrations of the 10 IRH in the RHM were between 0.42 to 0.45 mg/g (Tab. 2) resulting in a total of all compounds of 4.4221 mg/g.

3.3 Preparation of BAM-K009a test solutions

Five units of BAM-K009a were selected for the determination of the C₁₀-C₄₀ mass fraction (equally distributed over the whole batch of 622 units: No. 080, 190, 300, 420 and 550). Five test solutions were gravimetrically prepared from each selected BAM-K009a unit in n-heptane (concentration about 16 mg/g) resulting in 5 x 5 = 25 measurement solutions. A BAM-K009a concentration of about 16 mg/g was defined based on GC-FID pre-tests including the RHM solution. The pre-tests aimed to find out comparable FID signals between BAM-K009a solution and RHM solution to ensure equal sensitivity/response.

3.4 GC-FID measurements and integration

All measurements were performed using an Agilent 7890 gas chromatographic system equipped with a flame ionization detector (FID). The Agilent OpenLab software was used for measurement and system control as well as for data evaluation. Two separate measurement series were recorded using column A and B (Tab. 3).

Tab. 3: GC-FID conditions for measurements of the C₁₀-C₄₀ mass fraction of BAM-K009a

	Column A	Column B
GC capillary column	BPX-5: 12 m x 0.32 mm x 1 µm (SGE)	BP-1: 12 m x 0.32 mm x 1 µm (SGE)
Internal column-no.	#104	#106
Guard column	Deactivated fused silica: 5 m x 0.53 mm (Agilent)	
On-column injection	2 µL	
Carrier gas: N ₂ (5.0)	3 mL/min	
FID gases	Synthetic air: 400 mL/min; Hydrogen (5.0): 40 mL/min; Make-up gas N ₂ (5.0): 40 mL/min	
FID temperature	370°C	340°C
Oven program	60°C (5 min) → 360°C (5min)	60°C (5 min) → 330°C (5min)
Heating rate:	10 °C/min	15 °C/min

The following solutions were analysed in randomized order on both GC-FID systems (column A and B):

- 2 vials of n-alkanes mix in heptane for retention time setting of C₁₀ and C₄₀
- 25 BAM-K009a vials analysed in duplicate (50 injections)
- 6 RHM vials analysed in triplicate (18 injections)
- 12 vials of n-heptane (blanks) analysed in duplicate (24 injections)

At first, a n-alkanes mix containing 31 homologues between C₁₀ and C₄₀ was analysed to define the start/stop retention times for C₁₀ (start: at the end of the n-decane peak) and C₄₀ (stop: at the beginning of the n-tetracontane peak), see Fig. 1. These retention time marks were used to integrate all samples analysed with the same conditions.

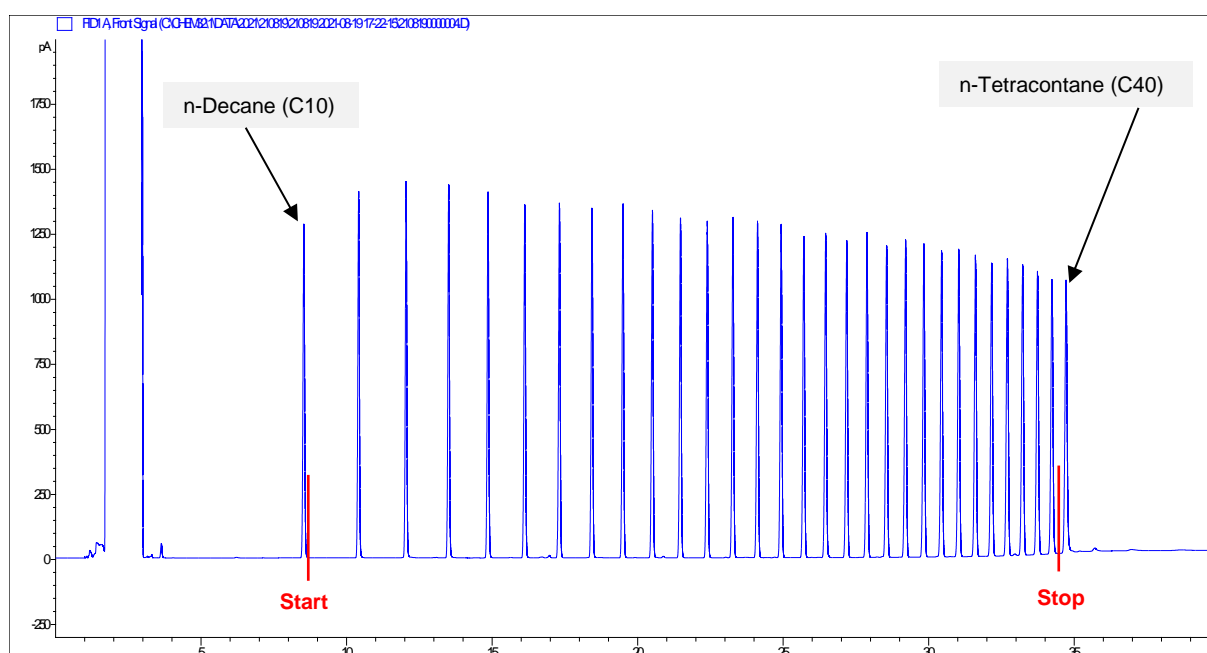


Fig. 1: GC-FID chromatogram of a n-alkanes mix containing 31 homologues between C₁₀ and C₄₀, analyzed on a BPX-5 column to define the start/stop retention times

Afterwards, the chromatograms of BAM-K009a and the pure solvent n-heptane (blank) were integrated between the start/stop marks determined before (Fig. 2, 3). The baseline was set at the level before the solvent peak acc. to the integration procedures of the standard methods [1, 2, 3].

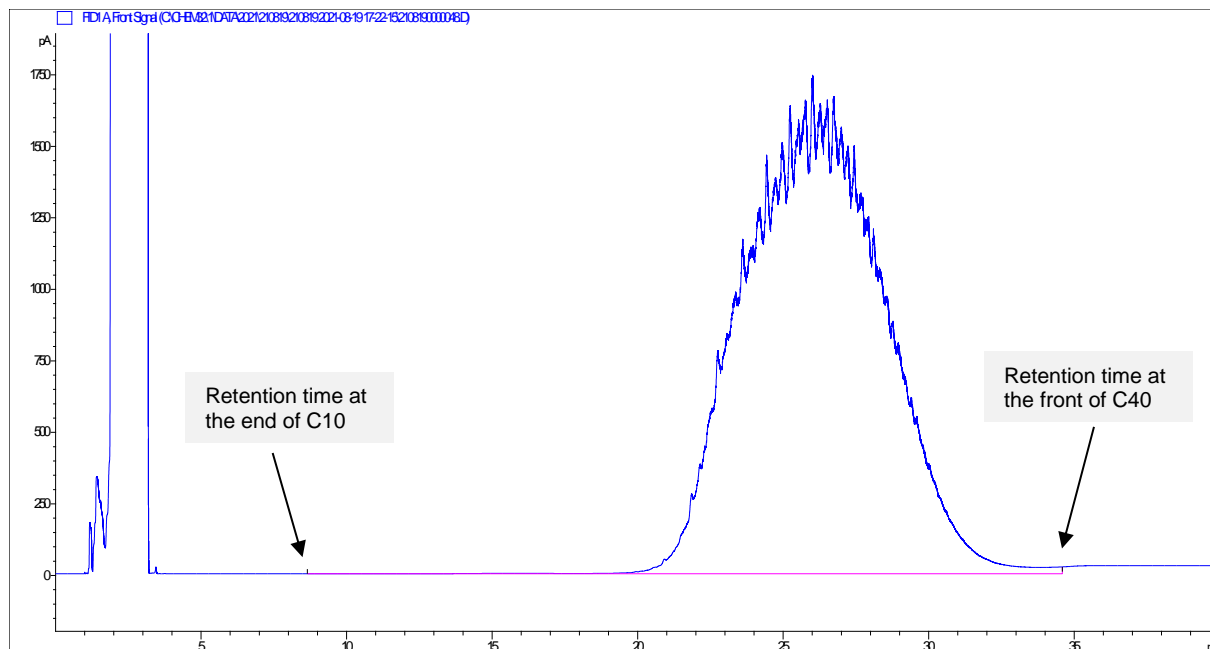


Fig. 2: Integrated GC-FID chromatogram of BAM-K009a (No. 080) between the retention times of C₁₀ and C₄₀ (analyzed on a BPX-5 column)



Fig. 3: Integrated GC-FID chromatogram of n-heptane (blank, pure solvent used to prepare BAM-K009a solutions) between the retention times of C₁₀ and C₄₀ (analyzed on a BPX-5 column)

The RHM chromatograms were not integrated over the broad range between C₁₀-C₄₀ to avoid the integration of substances' impurities. Instead, all 10 IRHs in the RHM-chromatogram were separately integrated (Fig. 4).

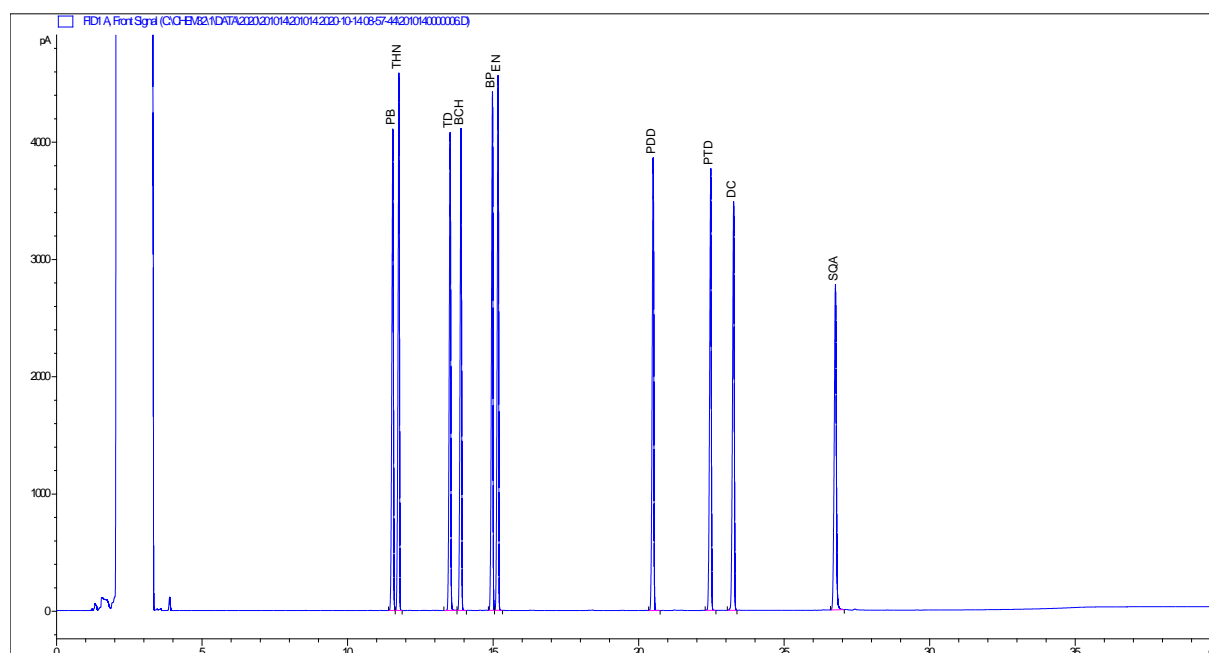


Fig. 4: GC-FID chromatogram of the reference hydrocarbon mixture (RHM) analyzed on a BPX-5 column; all 10 individual reference hydrocarbons (IRH) are integrated separately

3.5 Calculation of the C₁₀-C₄₀ mass fraction

As described in section 3.1, the determination of the C₁₀-C₄₀ mass fraction is based on the general principal of equal FID-responses of BAM-K009a and reference hydrocarbon mixture according to Eq. 3:

$$R_{MKW} = R_{RHM} \quad \text{Eq. 3}$$

The FID response is defined as the ratio of the detector signal (peak area) to the injected mass of a substance or mixture. Because the injected mass (in pico- to nanogram range) is unusual to handle, the concentrations of RHM- and BAM-K009a solutions are used in the following equations (more precisely the mass fraction (mg/g) of the solutions), Eq. 4. This approach requires a constant injection volume (2 µL) and the same type of solvent for all samples to be compared (n-heptane).

$$R_{MKW} = R_{RHM} = \frac{A_{MKW}^{total}}{c_{MKW}^{total}} = \frac{A_{RHM}}{c_{RHM}} \quad \text{Eq. 4}$$

A_{MKW}^{total}

total peak area of a BAM-K009a solution after blank correction (n-heptane),
not determined

c_{MKW}^{total}	concentration of a BAM-K009a solution in n-heptane based on gravimetric preparation (representing a defined mass of BAM-K009a injected into the GC-FID system)
A_{RHM} analysis)	mean value of the peak areas of 18 RHM analyses (sum of 10 IRH for each analysis)
c_{RHM}	concentration of the RHM solution, i.e. sum of 10 IRH conc. in RHM solution (representing a defined mass of 10 IRH injected into the GC-FID system)

Because BAM-K009a is a complex mixture of many hydrocarbons (representing different types of hydrocarbons) it can be presumed that the FID response of the C₁₀-C₄₀ mass fraction is comparable to the FID response of all compounds of BAM-K009a (Eq. 5):

$$\frac{A_{MKW}^{total}}{c_{MKW}^{total}} = \frac{A_{MKW}^{C_{10}-C_{40}}}{c_{MKW}^{C_{10}-C_{40}}} \quad \text{Eq. 5}$$

$A_{MKW}^{C_{10}-C_{40}}$	peak area of BAM-K009a between C ₁₀ -C ₄₀ after blank correction (n-heptane)
$c_{MKW}^{C_{10}-C_{40}}$	concentration of a BAM-K009a solution for C ₁₀ -C ₄₀ fraction (representing a defined mass of BAM-K009a's C ₁₀ -C ₄₀ fraction injected into GC-FID system)

Based on Eq. 4 and Eq. 5 the concentration of the C₁₀-C₄₀ fraction of a BAM-K009a solution is determined using Eq. 6:

$$c_{MKW}^{C_{10}-C_{40}} = \frac{A_{MKW}^{C_{10}-C_{40}}}{A_{RHM}} * c_{RHM} \quad \text{Eq. 6}$$

The final mass fraction of the C₁₀-C₄₀ boiling range is defined as the ratio of the calculated C₁₀-C₄₀ concentration of BAM-K009a to the total concentration of BAM-K009a based on gravimetric preparation (Eq. 7). As the concentrations represent the injected masses (see explanation above), $w_{MKW}^{C_{10}-C_{40}}$ is the C₁₀-C₄₀ mass fraction (g/g) of BAM-K009a.

$$w_{MKW}^{C_{10}-C_{40}} = \frac{c_{MKW}^{C_{10}-C_{40}}}{c_{MKW}^{total}} = \frac{m_{MKW}^{C_{10}-C_{40}}}{m_{MKW}^{total}} \quad \text{Eq. 7}$$

$m_{MKW}^{C_{10}-C_{40}}$	mass of BAM-K009a between C ₁₀ -C ₄₀ (exp. determined by GC-FID)
m_{MKW}^{total}	total mass of BAM-K009a (from gravimetric preparation)

Table 4 contains the C₁₀-C₄₀ mass fractions of BAM-K009a resulting from analysis of five units (25 sub-units) on two different GC-columns.

Tab. 4: C₁₀-C₄₀ mass fraction of BAM-K009a; each value represents the mean of 10 results (5 sub-units per unit, two results per sub-unit)

GC-column	C ₁₀ -C ₄₀ mass fraction (g/g)					GC-Column mean
	Unit 080	Unit 190	Unit 300	Unit 420	Unit 550	
A (BPX-5)	0.9816	0.9836	0.9802	0.9846	0.9800	0.9820
B (BP-1)	0.9831	0.9809	0.9816	0.9822	0.9811	0.9818
Mean of unit	0.982	0.982	0.981	0.983	0.981	
Mean (exact)	0.9819					
Mean (rounded)	0.982					

The mean (exact) is the average of the two GC-column means. The rounded mean value from Tab. 4 being 0.982 g/g was taken as the assigned (= certified) C₁₀-C₄₀ mass fraction of BAM-K009a.

4. Homogeneity

An excellent level of homogeneity was expected for BAM-K009a based on the unlimited miscibility of the hydrocarbon components in the liquid diesel oil without additives. In addition, the same diesel oil was used to produce BAM-K010g and no inhomogeneity effects were observed with respect to the diesel component. It should be kept in mind that there is no analytical method available that is precise enough to detect minimal inhomogeneities of a pure diesel oil (other properties than the C₁₀-C₄₀ mass fraction are not suitable). However, the determination of C₁₀-C₄₀ mass fractions by GC-FID was used at least to demonstrate "between-unit homogeneity" or to detect major inhomogeneities, knowing that the measurement method is of limited suitability for this purpose. From each of the five BAM-K009a units, five independent dilutions in n-heptane were prepared and directly analyzed by GC-FID using a BPX-5 and BP-1 column. The mean values of both columns displayed in Tab. 5 were used for ANOVA evaluation (Tab. 6).

Tab. 5: Mean values of the C₁₀-C₄₀ mass fraction of selected units of BAM-K009a resulting from analyses on BPX-5 and BP-1 column

sub-unit	C ₁₀ -C ₄₀ mass fraction (g/g)				
	Unit 080	Unit 190	Unit 300	Unit 420	Unit 550
1	0.986	0.990	0.982	0.979	0.977
2	0.981	0.977	0.982	0.987	0.986
3	0.982	0.980	0.985	0.977	0.977
4	0.977	0.985	0.976	0.984	0.984
5	0.986	0.979	0.980	0.990	0.979

Tab. 6: One-factorial ANOVA results from homogeneity study of BAM-K009a ($\alpha = 0.05$)

Source of variability	sum of squares (SS)	degrees of freedom (df)	mean squares (MS)	test statistic (F)	P value	critical value
differences between groups	2.6895E-05	4	6.7238E-06	0.34953	0.84123	2.86608
differences within groups	3.8473E-04	20	1.9237E-05			
total	4.1163E-04	24				

As assumed, the test criterion (F) is less than the critical value, which means that there is no significant inhomogeneity between units (significance level α , $\alpha = 0.05$). Furthermore, because $MS_{between} < MS_{within}$ the calculation of an inhomogeneity contribution (u_{bb}) according to ISO Guide 35 is not applicable. Therefore, u_{bb} is set to zero and no contribution of homogeneity was included in the uncertainty budget.

5. Stability

Chemical stability: Experiences from about 20 years of BAM-K009 have shown that the neat lubricating oil is chemically stable stored at room temperature in a dark place. Therefore, no further investigations regarding the chemical stability were done.

Tightness of the units: Due to certain vapor pressure of the lubricating oil, leakage tests of the BAM-K009a vials were performed over 3, 6, 9 and 12 months at room temperature with 3 vials standing upright, 3 vials stored horizontally, and 3 vials stored upside down. Outcome: The average mass loss after 12 months was 0.01 % showing no significant differences between the three storage positions of the vials. The leakage tests will be continued on a regular basis.

6. Uncertainty

The overall uncertainty of the $C_{10}-C_{40}$ mass fraction of BAM-K009a ($u_{MKW}^{C_{10}-C_{40}}$) results from combining a "within method" contribution u_{MKW}^{wm} and a "between method" contribution u_{MKW}^{bm} according to Eq. 8.

$$u_{MKW}^{C_{10}-C_{40}} = \sqrt{(u_{MKW}^{wm})^2 + (u_{MKW}^{bm})^2} \tag{Eq. 8}$$

Uncertainty due to "within method" contribution:

The terms contributing to the "within method" uncertainty u_{MKW}^{wm} are displayed in Eq. 9, which results from inserting Eq. 6 into Eq. 7:

$$w_{MKW}^{C_{10}-C_{40}} = \frac{A_{MKW}^{C_{10}-C_{40}} * c_{RHM}}{A_{RHM} * c_{MKW}^{total}} \tag{Eq. 9}$$

The concentration of the RHM-solution (c_{RHM}) is influenced by the weighing processes for preparation of the IRH- and RHM-solutions and the IRH-purities. However, the corresponding uncertainty does not contain the uncertainty of the 10 IRH purities. Therefore, an additional “within method” contribution due to RHM purity (f_{pur}) has to be taken into account. According to GUM [8] the combined standard uncertainty $u_c(y)$ is the positive square root of the combined variance $u_c^2(y)$, which is given by Eq. 10

$$u_c^2(y) = \sum_{\{i=1\}}^N \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) \quad \text{Eq. 10}$$

That means, partial derivatives of Eq. 9 according to the uncertainty related terms x_i ($A_{MKW}^{C10-C40}$, c_{RHM} , A_{RHM} , c_{MKW}^{total}) and f_{pur} have to be performed, displayed in the following Eq. 11 to Eq. 15.

Partial derivative with respect to BAM-K009a concentration (c_{MKW}^{total}):

$$\frac{\partial f}{\delta c_{MKW}^{total}} = - \frac{A_{MKW}^{C10-C40} * c_{RHM}}{A_{RHM} * (c_{MKW}^{total})^2} \quad \text{Eq. 11}$$

Partial derivative with respect to RHM concentration (c_{RHM}):

$$\frac{\partial f}{\delta c_{RHM}} = \frac{A_{MKW}^{C10-C40}}{A_{RHM} * c_{MKW}^{total}} \quad \text{Eq. 12}$$

Partial derivative with respect to RHM peak area normalized to c_{RHM} ($u_{A_{RHM}/c_{RHM}}$):

$$\frac{\partial f}{\delta A_{RHM}/c_{RHM}} = - \frac{A_{MKW}^{C10-C40}}{c_{MKW}^{total}} * \left(\frac{c_{RHM}}{A_{RHM}} \right)^2 \quad \text{Eq. 13}$$

Partial derivative with respect to BAM-K009a peak area normalized to c_{MKW} ($u_{A_{MKW}/c_{MKW}}$):

$$\frac{\partial f}{\delta A_{MKW}/c_{MKW}} = \frac{c_{RHM}}{A_{RHM}} \quad \text{Eq. 14}$$

Partial derivative with respect to uncertainty of RHM purity (f_{pur}) based on c_{RHM} :

$$\frac{\partial f}{\delta c_{RHM}} = \frac{A_{MKW}^{C10-C40}}{A_{RHM} * c_{MKW}^{total}} \quad \text{Eq. 15}$$

For both GC-columns a “within method” uncertainty (u_{MKW}^{wm-col}) was determined. The uncertainty contributions and calculated results are displayed in Tab. 7 for BXP-5 and in Tab. 8 for BP-1 column.

Tab. 7: "Within method" uncertainty of C₁₀-C₄₀ mass fraction of BAM-K009a for BPX-5

Uncertainty contribution		value	uncertainty	df/d _{xi}	(df/d _{xi}) ² *u ² (x _i)
Uncertainty of BAM-K009a concentration (gravimetric preparation) based on uncertainty estimation from weighing BAM-K009a and solvent (0.2 %) including evaporation effects.	u_c^{MKW}	16.2290 mg/g	0.0325 mg/g	- 0.060507 616	3.85712E-06
Uncertainty of RHM concentration (gravimetric preparation) based on uncertainty estimation from weighing 10 IRHs and solvent (0.4 %) including evaporation effects.	u_c^{RHM}	4.4221 mg/g	0.0177 mg/g	0.219983 522	1.51408E-05
Uncertainty of RHM purity (combined uncertainty of 10 IRH purity uncertainties acc. to Eq. 2)	u_{pur}	4.4221 mg/g	0.0088 mg/g	0.219983 522	3.72173E-06
Uncertainty of RHM peak area (standard deviation of the mean of 18 RHM analyses) normalised to the RHM concentration	$u_{A/c}^{RHM}$	34793.239 (counts*g/mg)	78.957 (counts*g/mg)	- 2.82232E -05	4.96592E-06
Uncertainty of BAM-K009a peak area (standard deviation of the mean of 50 BAM-K009a analyses) normalised to the concentration of specific BAM-K009a solution	$u_{A/c}^{MKW}$	34166.202 (counts*g/mg)	39.195 (counts*g/mg)	2.87412E -05	1.26904E-06
Uncertainty of the C ₁₀ -C ₄₀ mass fraction (g/g)	$u_{MKW}^{wm_BPX5}$	0.0046			

Tab. 8: "Within method" uncertainty of C₁₀-C₄₀ mass fraction of BAM-K009a for BP-1

Uncertainty contribution		value	uncertainty	df/d _{xi}	(df/d _{xi}) ² *u ² (x _i)
Uncertainty of BAM-K009a concentration (gravimetric preparation) based on uncertainty estimation from weighing BAM-K009a and solvent (0.2 %) including evaporation effects.	u_c^{MKW}	16.2290 mg/g	0.0325 mg/g	- 0.060496 391	3.85569E-06
Uncertainty of RHM concentration (gravimetric preparation) based on uncertainty estimation from weighing 10 IRHs and solvent (0.4 %) including evaporation effects.	u_c^{RHM}	4.4221 mg/g	0.0177 mg/g	0.221977 895	1.54166E-05
Uncertainty of RHM purity (combined uncertainty of 10 IRH purity uncertainties acc. to Eq. 2)	u_{pur}	4.4221 mg/g	0.0088 mg/g	0.221977 895	3.78952E-06
Uncertainty of RHM peak area (standard deviation of the mean of 18 RHM analyses) normalised to the RHM concentration	$u_{A/c}^{RHM}$	33475.301 (counts*g/mg)	18.886 (counts*g/mg)	-2.9329E -05	3.0681E-07

Uncertainty of BAM-K009a peak area (standard deviation of the mean of 50 BAM-K009a analyses) normalised to the concentration of specific BAM-K009a solution	$u_{A/c}^{MKW}$	32865.918 (counts*g/mg)	19.107 (counts*g/mg)	2.98728E-05	3.25775E-07
Uncertainty of the C ₁₀ -C ₄₀ mass fraction (g/g)	$u_{MKW}^{wm_BP1}$	0.0047			

The final uncertainty due to “within method” contribution was calculated to 0.0051 g/g based on Eq. 16 by inserting the values from Tab. 7 and Tab. 8.

$$u_{MKW}^{wm} = \sqrt{\frac{(u_{MKW}^{wm_BPX5})^2 + (u_{MKW}^{wm_BP1})^2}{2}} \tag{Eq. 16}$$

Uncertainty due to “between method” contribution:

The “between method” uncertainty contribution u_{MKW}^{bm} is due to the difference of the C₁₀-C₄₀ mass fractions determined by BPX-5 and BP-1 column (comparable to different laboratory mean values from a certification study). A one-factorial ANOVA was performed based on the values displayed in Tab. 4 with two methods (BPX-5, BP-1) and 5 units (n=5) as factors. The final uncertainty due to “between method” contribution is calculated acc. to Eq. 17a or, alternatively, acc. to Eq. 17b if $MS_{between} < MS_{within}$. u_{MKW}^{bm} was determined to 0.0005 g/g.

$$u_{MKW}^{bm} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \tag{Eq. 17a}$$

$$u_{MKW}^{bm} = \sqrt{\frac{MS_{within}}{n}} * \sqrt[4]{\frac{2}{N(n-1)}} \tag{Eq. 17b}$$

Overall uncertainty:

The overall uncertainty of the C₁₀-C₄₀ mass fraction of BAM-K009a $u_{MKW}^{C10-C40}$ was calculated by combining the “within method” contribution u_{MKW}^{wm} and the “between method” contribution u_{MKW}^{bm} according to Eq. 8 resulting to $u_{MKW}^{C10-C40} = 0.0052$ g/g.

The expanded uncertainty $U_{MKW}^{C10-C40}$ was calculated acc. to Eq. 18 applying a coverage factor of k=2:

$$U_{MKW}^{C10-C40} = k * u_{MKW}^{C10-C40} \tag{Eq. 18}$$

The expanded uncertainty of $U_{MKW}^{C10-C40} = 0.0103$ g/g was rounded up to 0.011 g/g.

7. Certified value of BAM-K009a

The certified mass fraction of the boiling range between decane (C₁₀) and tetracontane (C₄₀) and its corresponding expanded uncertainty (k=2) is: 0.982 ± 0.011 g/g.

8. Metrological Traceability

The mass fraction of the boiling range C₁₀ - C₄₀ is traceable to a hydrocarbon reference mixture consisting of ten hydrocarbon standards (Sigma-Aldrich) with defined and confirmed purities through direct comparisons using gas chromatography with flame ionisation detection (GC-FID) and gravimetric handling. Accurate weighing is ensured using a calibrated balance.

9. Information on proper use of BAM-K009a

9.1 Transport, storage, handling and use

Intended use: The certified reference material BAM-K009a is intended to be used as a type B mineral oil of a calibration standard for the gas chromatographic determination of mineral oil hydrocarbons in water, soil and waste according to the analytical standard procedures ISO 9377-2, ISO 16703 and EN 14039.

Handling: Proper use of the reference material is essential for avoiding potential harm to the user. It is strongly recommended to handle and dispose of the reference material in accordance with the guidelines for hazardous materials legally in force at the site of end use and disposal. The content of the vial is preferably used completely at once. If not, the vial should be re-sealed with a new crimp cap or remaining standard should be filled in a tightly closed glass container and stored as specified.

Transport, Storage: Due to the proved stability a cooled dispatch of BAM-K009a is not necessary. On receiving, BAM-K009a is to be stored tightly closed at room temperature in a dark place. Under these storage conditions the material remains clear. If the material should become turbid by time, it should be replaced by a fresh unit and storage conditions should be checked and adjusted.

9.2 Shelf life

From stability monitoring a shelf life of at least 20 years is estimated for the storage of BAM-K009a at room temperature in a dark place. Since the dispatch to the end user may occur at any time, the certificate is valid for a period of two years beginning with the dispatch of the reference material from BAM. The validity of this information will be maintained by post-certification monitoring.

9.3 Legal notice

Neither BAM, its contractors nor any legal person acting on their behalf:

- (a) make any warranty or representation, express or implied, that the use of any information, material, apparatus, method or process disclosed in this document does not infringe any privately owned intellectual property rights; or
- (b) assume any liability with respect to, or for damages resulting from the use of any information, material, apparatus, method or process disclosed in this document save for loss or damage arising solely and directly from the negligence of BAM.

10. Information on and purchase of the CRM

The certified reference material BAM-K009a is supplied by

Bundesanstalt für Materialforschung und -prüfung (BAM)
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Division 1.7 - Organic Trace and Food Analysis
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Phone: +49 30 8104 2061
Fax: +49 30 8104 72061
E-Mail: sales.crm@bam.de

Each unit of BAM-K009a will be distributed together with a detailed certificate containing the certified value and its uncertainty, a material description and information on recommend use, handling, storage and metrological traceability.

Information on certified reference materials can be obtained from BAM homepage <https://www.bam.de> and BAM-webshop www.webshop.bam.de.

11. References

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- [5] ISO Guide 31 (2015), Reference materials - Contents of certificates, labels and accompanying documentation.
- [6] ISO Guide 35 (2017), Reference materials - Guidance for characterization and assessment of homogeneity and stability.
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- [8] JCGM 100:2008, GUM 1995 with minor corrections, Evaluation of measurement data – Guide to the expression of uncertainty in measurement. Joint Committee for Guides in Metrology (JCGM/WG 1).