Federal Institute for Materials Research and Testing

CERTIFICATION REPORT

Mineral oil calibration standard in n-heptane

Certification of the mass fraction of the boiling range C_{10} to C_{40}

ausverkauft / out of stock

Certified Reference Material

BAM-K011

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Berlin, September 2012

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SUMMARY

This report describes the certification of a mineral oil reference material used as calibration standard for the analytical procedures ISO 9377-2 (2000), ISO 16703 (2004) and EN 14039 (2004) for the gas chromatographic determination of mineral oil hydrocarbons in water, soil and waste. Detailed information is given related to material preparation, homogeneity and stability studies, the used analytical methods and the results of the certification process. The certified value and its uncertainty are:

Mineral oil hydrocarbons in n-heptane		
Characteristic	Certified value [1] in mg g^{-1}	Uncertainty U [2] in mg g^{-1}
Mass fraction of the boiling range C_{10} – C_{40}	14.71	0.32

[1] The certified mass fraction (mg g^{-1}) corresponds to a concentration of 10.00 mg mL^{-1} based on the density ρ of n-heptane of $\rho = 0.68$ g cm^{-3} at 23 °C. The certified value is based on gravimetric preparation supported by instrumental verification and is directly traceable to the SI.

[2] Expanded uncertainty U with a coverage factor of $k = 2$, corresponding to a level of confidence of about 95 % according to ISO/IEC Guide 98-3 (2008) Uncertainty of measurement—part 3: guide to the expression of uncertainty in measurement (GUM:1995). International Organization for Standardization (ISO), Geneva.

LIST OF ABBREVIATIONS

(if not explained elsewhere)

ANOVA	Analysis of Variance
CoA	Certificate of Analysis
CRM	Certified reference material
FID	Flame ionization detector / detection
GC	Gas chromatography
GUM	Guide to the expression of uncertainty in measurement
ISO	International Organization of Standardization
k	reaction rate
k	coverage factor
K	Kelvin
TPH	Total petroleum hydrocarbons

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1 Introduction

Mineral oils (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. Due to their large scale handling, accidents and spills during production, transport and use lead to environmental contaminations, particularly related to water and soil compartments. Due to serious, adverse ecologic and 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.

Validated methods already existing for the determination of TPH in water, soil and waste (ISO 9377-2 (2000), ISO 16703 (2004) and EN 14039 (2004)) are based on gas chromatography coupled to flame ionization detection (FID).
Reference materials and especially certified reference materials (CRM) are versatile tools to verify the accuracy of analytical measurements. Certified matrix-CRMs for soil and waste (e.g. ERM-CC017) and neat calibration standards (e.g. BAM-K010) for TPH analysis are already commercially available. However, a *ready-to-use* calibration standard – not available at present - is often requested by costumers of BAM's reference materials. Such calibration standard provides the basis for accurate measurements, facilitates the laboratory work and saves time. Therefore, a new certified reference material (BAM-K011) for calibration according to the above mentioned standard methods was developed at BAM.

The reference material BAM-K011 was produced to be utilized as a TPH stock solution for the preparation of further calibration standards by dilution with appropriate solvents. BAM-K011 is a n-heptane based solution containing BAM-K010c, a certified mixture of additive free diesel and lubricating oil (1:1, w:w) including the retention time marker compounds n-decane ($C_{10}H_{22}$; "C_{10}") and n-tetracontane ($C_{40}H_{82}$; "C_{40}").

This report describes the preparation, characterization and certification of the calibration standard including the homogeneity and stability studies. The certified mass fraction of TPH, its uncertainty and the shelf life were evaluated according to internationally accepted procedures.

2 Time schedule for RM preparation and characterization

The whole process of material preparation, characterization and certification is summarized in Table 1.

Tab. 1: Time schedule for the development of BAM-K011

Process	Completed	Comment
Preparation	05/2007	Derived from BAM-K010c
Homogeneity	05/2007	6 Vials out of 200 vials tested in triplicate
Stability study	08/2008	Stability monitored over 6 months at 4°C, 23°C and 40°C (reference temperature: -20°C)
Stability monitoring	09/2011	Preparation of a “fresh” K011 solution and comparison to three vials of K011 prepared in 05/2007
Certification	05/2012	Acceptance of the CoA by BAM certification committee

3 Production of the candidate material

3.1 Preparation of the candidate material

All steps for the preparation of BAM-K011 were gravimetrically controlled using calibrated balances with appropriate mass ranges. Furthermore, atmospheric pressure (1015 ± 1) mbar, relative humidity (38 ± 3) % and temperature (22.5 ± 0.5) °C were recorded at start and end of the preparation process (mean values are given). Temperature was used for buoyancy correction.

The neat calibration standard BAM-K010c (lot no. IV from 11/2006) was used as the TPH component consisting of a diesel/lubricating oil mass ratio of 1.00003 ± 0.00006 and a boiling range (C_{10} – C_{40}) mass fraction of 0.967 ± 0.018.

a) **Weighing the TPH analyte (BAM-K010c)**; balance: Mettler Toledo AX205 Delta Range
   Balance verification was done using three calibrated weights (1 g, 10 g and 100 g) and combining them (1 to 110 g) to cover the range of analyte weighing.

Tab. 2: Weighing the TPH analyte (BAM-K010c)

analyte mass (g):			10,35803333						
balance range (g):			106						
balance verification			mass (g)		indication (g)				
			value	u(value)	value	u(value)	nominal	difference	u(diff)
			1,000005	0,00001	0,999948	2,3875E-05	1	5,7E-05	2,58844E-05
			10,000023	0,00002	9,999978	3,5637E-05	10	4,5E-05	4,08658E-05
			100,000001	0,00005	99,99988	4,4691E-05	100	0,000121	6,70615E-05
			110,000024	0,0000539	109,99998	8,3663E-05	110	4,4E-05	9,94961E-05
				g					
scale resolution (in the range):				0,00005					
buoyancy correction (0.09%):				0,00932223					
calibration uncertainty:				0,00006706					
calibration correction:				0,000121					
		total:		0,009323391					
	value	uncertainty	rel uncertainty						
	10,3580333	0,0093234	0,0009001						

b) Weighing the solvent (n-heptane); balance: Sartorius LP3200D

Balance verification was done using three calibrated weights (100 g, 500 g and 1000 g) and combining them (100 g to 1500 g) to cover the range of analyte weighing.

Tab. 3: Weighing the solvent (n-heptane)

full mixture mass (g):			681,03						
balance range (g):			963						
balance verification			mass (g)		indication (g)				
			value	u(value)	value	u(value)	nominal	difference	u(diff)
			100,000001	0,00005	99,9996	0,00089443	100	0,000401	0,000895824
			500,002	0,01	500,0008	0,00178888	500	0,0012	0,010158744
			1000,043	0,011	1000,043	0,00447213	1000	0	0,011874339
			1500,045	0,0148661	1500,046	0,00547725	1500	0,001	0,015842987
				g					
scale resolution (in the range):				0,00005					
buoyancy correction (0.14%):				0,953442					
calibration uncertainty:				0,01187434					
calibration correction:				0					
		total:		0,953515941					
	value	uncertainty	rel uncertainty						
	681,03	0,953515941	0,001400109						

For step b) the weighed mineral oil was transferred into a 1 L flask and rinsed several times with n-heptane. Afterwards, 21.9 mg (30 µL) of n-decane (liquid) and 30.6 mg of n-tetracontane (solid) were added to the 1 L flask. Finally, the flask was filled up to the mark and weighed.

c) TPH mass fraction of BAM-K011

The TPH mass fraction of BAM-K011 (uncorrected for the C_{10}/C_{40} boiling range mass fraction of BAM-K010) was calculated based on the weights of TPH analyte and solvent.

Tab. 4: TPH mass fraction of BAM-K011 in mg g^{-1}, uncorrected for C_{10}/C_{40} boiling range mass fraction

value	uncertainty	rel uncertainty
15,2093642	0,025315738	0,001664484

d) Bottling of BAM-K011

After rinsing the Certan® vials (Figure 1) with argon to expel oxygen from inside the vials a total of 200 vials were filled with BAM-K011 solution containing each (3.28 ± 0.02) g (about 4.5 mL).

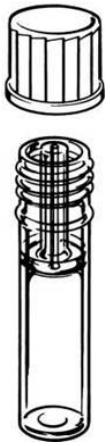

Fig. 1: Certan® vials (4.5 mL) used for bottling calibration standard BAM-K011

3.2 Gas chromatography (GC-FID)

Mineral oil hydrocarbons are measured by gas chromatography coupled to a flame ionization detector (GC-FID) according to the standard methods for water, soil and waste. The complex mixture of mineral oils consisting of hundreds of hydrocarbons will be separated according to their boiling points by using a non-polar GC-column. Therefore, this process is called 'simulated distillation'. To ensure a uniform and reproducible integration procedure two retention time marker (n-decane, 'C_{10}' and n-tetracontane, 'C_{40}') are included in the calibration solutions as well as in the sample extracts. The concentration of these markers should be about 30 mg L^{-1}. However, an exact match to this recommended concentration is not necessary because both substances will not be included in the integration (Figure 2).

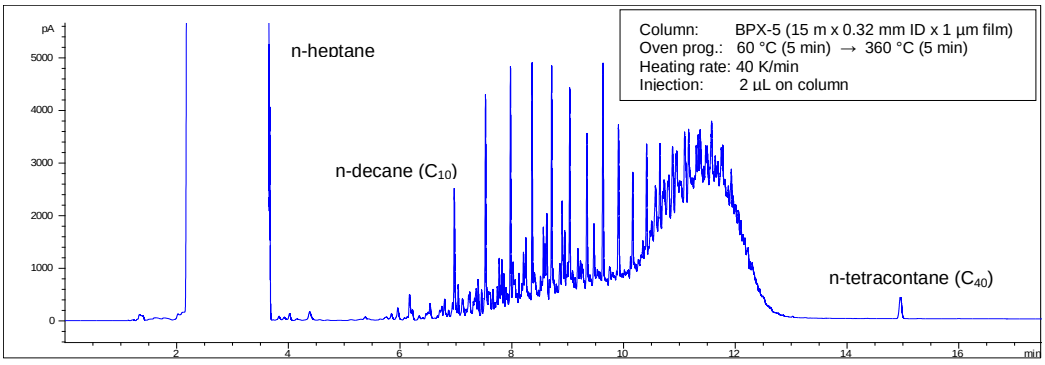

Fig. 2: GC-FID chromatogram of calibration standard BAM-K011

A FID is mandatory for TPH detection according to the convention laid down in ISO 9377-2 (2000), ISO 16703 (2004) and EN 14039 (2004) because the signal response, i.e. the ratio of signal area to mass of analyte, is comparable for different types of hydrocarbons. Other detectors, e.g. mass selective detectors (MSD), are generally possible but not suitable for quantitative TPH analysis.

All GC measurements for homogeneity, stability and stability monitoring were performed as stated in Table 5.

Tab. 5: Gas chromatographic conditions

	Instrument / Measurement conditions
GC	
Instrument	Agilent 6890
Column	BPX-5 (15 m x 0.32 mm ID x 1 µm film) (SGE)
Pre-column	Fused silica (5 m x 0.53 mm ID)
Carrier gas	Helium 5.0; flow rate: 3 mL min^{-1}
Make-up gas	Helium 5.0; flow rate: 45 mL min^{-1}
Oven program	60 °C (5 min isotherm) ---- 360 °C (5 min isotherm)
Heating rate	40 K min-1
Injection volume	2 µL (on-column)
FID detection	
FID temperature	370 °C
Flame gases	Synthetic air (450 mL min^{-1}), hydrogen 5.0 (40 mL min^{-1})
Software	Agilent ChemStation (version A09)

The performance of the GC-FID system (chromatographic resolution, FID sensitivity, degree of peak discrimination) was checked by applying a solution consisting of the homologous compounds of n-alkanes (C_8 to C_{40}) in the frame of routine control chart measurements. A calibration was not necessary for the intended purposes (homogeneity, stability).

4 Homogeneity study

A satisfactory level of homogeneity was expected based on an unlimited solubility of diesel/lubricating oil (1:1) in n-heptane. For further quantitative demonstration, 6 units were selected equally distributed over the whole set of 200 vials. The vials were analyzed three times each according to the GC-FID method described in section 3.2 under repeatability

conditions in a random order. The peak area ratio of TPH (between C_{10} and C_{40}) to n-tetracontane (C_{40}) was used to evaluate the homogeneity. Measurement results and ANOVA evaluation are displayed in Table 6 and Table 7, respectively.

Tab. 6: Peak area ratios of THP to C_{40} (arbitrary unit) of 6 randomly selected vials analyzed in triplicate (total mean peak area ratio: 347.0075).

ratio	replicate		
bottle	**1**	**2**	**3**
120	347,527587	350,253110	347,188680
160	349,579190	347,221336	343,792395
1	348,209725	349,914577	347,734673
200	346,423297	338,472665	343,321380
40	347,387593	349,601961	349,169111
80	345,606458	347,166140	347,565080

Tab. 7: ANOVA results from homogeneity measurements of BAM-K011

source of variability	*sum of squares (SS)*	*degree of freedom (df)*	*mean squares (MS)*	*test statistic*	*P value*	*critical value*
differences between groups	76,65836123	5	15,33167225	2,956937704	0,05749669	3,10587467
differences within groups	62,21979811	12	5,184983176			
total	138,8781593	17				

Because the test criterion is lower than the critical value, no significant inhomogeneity of the batch was detected. A contribution u_{bb} to the overall uncertainty of the certified reference material was nevertheless derived from the ANOVA results and included in the uncertainty budget of the certified value. The between-bottle (in)homogeneity standard deviation (s_{bb}) was calculated according to Equation 1, the minimum (s_{bb_min}) was determined by applying Equation 2.

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \qquad \textbf{(1)}$$

$$s_{bb_\min} = \sqrt{\frac{MS_{within}}{n}} \cdot \sqrt[4]{\frac{2}{df_{within}}} \qquad \textbf{(2)}$$

$MS_{between}$: mean of squared deviations between bottles

MS_{within}: mean of squared deviations within bottles

n: number of replicate analysis; n = 3

df_{within}: degrees of freedom (within groups); df_{within} = 12

The relative standard uncertainty due to between-bottle (in)homogeneity (u_{bb}) accounts to 0.53 % based on the higher value for s_{bb} (Table 8).

Tab. 8: Estimation of uncertainty due to between-bottle (in)homogeneity.

Uncertainty	value
s_bb	1,839083927
s_bb_min	0,839992166
u_bb	1,839083927
u_bb_rel	**0,005299839**

5 Stability study

5.1 Initial stability study

Selected units of the candidate material were submitted to accelerated ageing at temperatures between 4 °C and 40 °C over a period of 6 months as shown in Table 9 to perform a so-called isochronous stability study.

Tab. 9: Sample-no. of accelerated ageing for isochronous stability study

Ageing [months]	Storage temperature 4 °C	23 °C	40 °C
1	29	197	93
3	169	123	59
6	105	78	137

After the respective periods of time the exposed units were transferred into a freezer at -20 °C. All units were analyzed using the method described in section 3.2 under repeatability conditions together with 4 BAM-K011 reference samples which had been kept at -20 °C over the whole period of the initial stability study. The reference samples were evenly distributed over the whole measurement sequence and measured together with the exposed samples. From each Certan® vial three HPLC vials (with 1.5 mL content each) were filled and measured in duplicate (6 GC results per storage temperature and time).

Data processing and result assessment were carried out assuming an *Arrhenius* model. The data of *ln*(ratio), i.e. the peak area ratio of (TPH/C40) to reference, over the temperature is given in Table 10.

Tab. 10: Data of the 6 months initial stability study of BAM-K010 at 4, 23 and 40°C. The ratio refers to the peak area (TPH/C40) to the peak area of the reference standards stored at -20°C over the whole period of time.

4°C	months	ln(ratio)	23°C	months	ln(ratio)	40°C	months	ln(ratio)
	1	0,00584809		1	0,00125728		1	0,00068171
	1	0,00648189		1	-0,0002607		1	0,00025417
	1	0,00026344		1			1	-0,0015644
	1	-0,0024171		1	0,00712252		1	-0,0005956
	1	0,00319468		1	0,00231211		1	0,00262826
	1	0,00311833		1	0,00369279		1	0,00302024
	3	0,00993237		3	-0,002956		3	0,00104354
	3	0,01144081		3	0,00193287		3	-5,487E-06
	3	0,00146684		3	-0,0030047		3	0,00774975
	3	-0,0007974		3	0,00163799		3	0,00214811
	3	-0,0006327		3	-0,0021066		3	
	3	-0,0040069		3	-0,0009995		3	
	6	0,0129615		6			6	
	6	0,0026612		6	-0,0034823		6	0,00203293
	6	4,6732E-05		6	-0,0026659		6	-0,002568
	6	0,00261227		6	-0,0014814		6	-3,139E-05
	6	0,00918342		6	-0,0026389		6	
	6			6	-0,0009249		6	-0,0002927
intercept		0,00181905			0,00302627			0,00160711
slope		**0,00056358**			**-0,000962**			**-0,0001904**

The slopes of the calculated regression lines in Table 10 correspond to the reaction rate k. No clear conclusion could be drawn from the data in Table 10 showing the largest impact for 23 °C. However, common sense suggests the highest temperature to give the most reliable estimate. That means the reaction rate at 40 °C, k = 0.0001904 month^{-1} was taken for shelf life estimation. For any storage temperature below 40 °C, this implies a shelf life of 115 months. Consequently, no problems for delivery at 'normal' environmental conditions are to be expected.

5.2 Stability monitoring

From long year experiences it was known that the neat calibration standard BAM-K010 (diesel/lubricating oil 1:1) is chemically stable stored at room temperature at a dark place. In order to verify also the stability of BAM-K011, a fresh dilution of BAM-K010 in n-heptane was prepared in 09/2011 with a concentration similar to that of BAM-K011 prepared in 05/2007.

Fresh solution of BAM-K010 in n-heptane (09/2011): 14.852 mg g^{-1}

BAM-K011 (05/2007): 15.209 mg g^{-1}

The fresh solution was analyzed by GC-FID together with three vials of BAM-K011 (vial-no. 23, 114, 156). At first, the comparability of the BAM-K011 vials was confirmed by ANOVA (Table 11) as prerequisite to pool the data for further evaluation.

Tab. 11: ANOVA evaluation of BAM-K011 data (vials-no. 23, 114, 156) for stability monitoring

source of variability	*sum of squares (SS)*	*degree of freedom (df)*	*mean squares (MS)*	*test statistic (F)*	*P value*	*critical value*
differences between groups	4072965661	3	1357655220	0,020569758	0,99570074	3,86253873
differences within groups	5,94022E+11	9	66002487653			
total	5,98095E+11	12				

A mean concentration of 15.327 mg g^{-1} for BAM-K011 was obtained (100.77 % of the value from preparation in 05/2007) by setting the fresh solution to 100 %. After data evaluation it was shown that the verification result from 09/2011 (15.327 mg g^{-1}) is covered by the gravimetric preparation process of BAM-K011 in 05/2007 (see Section 6.1)

5.3 Post certification monitoring

The data of the initial stability study will be updated during a post-certification monitoring over the whole period of material's availability by GC-FID analyses and gravimetric control of the Certan® vials as well.

6 Certified value and traceability

6.1 Data evaluation

The data derived from gravimetric preparation, homogeneity and stability studies as well as stability monitoring (verification) are listed in Table 12.

Tab. 12: Summary of data analyzed for BAM-K011

in mg/g	value in mg g^{-1}	u(value) in mg g^{-1}
gravimetry	15,20936425	0,025315738
inhomogeneity		0,080609631
instability		0
before verification	15,20936425	0,084491414
verification	15,32699321	0,08407074
verification bias:		0
before correction	15,20936425	0,084491414
K010 absolute content correction	14,70745523	0,15941367
certified value and U(value)	14,70745523	0,31882734
rounded:	**14,71**	**0,32**

The uncertainty of BAM-K011 (before verification) was calculated including the uncertainty terms due to gravimetry and inhomogeneity. It was shown that the verification is covered by gravimetry, so the gravimetric value was taken for further evaluation. The TPH-content of BAM-K011 and the corresponding uncertainty had to be corrected by the mass fraction of BAM-K010 boiling range C_{10} – C_{40}, (0.967 ± 0.018) g g^{-1}. After applying a coverage factor *k* of *k* = 2 the rounded certified TPH-content of BAM-K011 resulted to (**14.71 ± 0.32) mg g^{-1}**.

By assuming a density of BAM-K011 equal to that of n-heptane (ρ = 0.68 g mL^{-1} at room temperature; Gestis Stoffdatenbank, 2010, http://gestis.itrust.de) a TPH-concentration of (**10.00 ± 0.22) mg mL^{-1}** can be given as information.

6.2 Metrological Traceability

The mineral oil mass fraction is traceable to the certified mass fraction of BAM-K010c used for the preparation of BAM-K011. The certification of BAM-K011 is based on precise weighing of the mineral oil component (BAM-K010c) and solvent (n-heptane) to be mixed.

Balance verification was performed and a correction of buoyancy has been applied. The gravimetric value is fully supported by instrumental verification.

7 Information on the proper use of BAM-K011

7.1 Shelf life

From the initial stability study, a material shelf life of 115 months was estimated based on a storage temperature lower than 40 °C. Since the dispatch to the end user may occur at any time during this period the certificate of analysis (CoA) will be valid for 12 months beginning with the dispatch of the material from BAM. The validity of this information will be maintained by post-certification monitoring.

7.2 Transport, storage and use

Due to the proved stability a cooled dispatch of BAM-K011 is not necessary. On receiving, the CRM unit is to be stored at room temperature at a dark place. Under these storage conditions the material remains colourless and clear. A cooled storage does not affect the stability but could lead to a precipitation of the n-tetracontane marker, which has to be re-dissolved before taking a sub-sample. In every case, before taking a sub-sample the vial should be allowed to reach room temperature. Thereafter, the bottle must be closed tightly and stored at room temperature. If the material should become turbid by time, it should be replaced by a fresh unit and storage conditions should be checked and adjusted.

7.3 Safety instructions

No hazardous effects are to be expected when the material is used under conditions usually adopted for the analysis of mineral oil hydrocarbons. 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.

7.4 Legal notice

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