

**BAM-U026**  
**Mineral oil contaminated soil**  
**Certification Report**

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Date: December 2023

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## 1 Introduction

Mineral oils are among the most abundant organic pollutants in environmental compartments and standardised procedures for the determination of total petrol hydrocarbons (TPH) in soil, water and waste have been developed [1-3]. Consequently, quality assurance in routine laboratories requires reference materials for proficiency testing [4, 5] and certified reference materials for method verification [6].

As a matter of fact, environmental contamination with mineral oil hydrocarbons originates from fossil fuels or related products such as lubricants. Therefore, complex mixtures of hydrocarbons are observed in practise and the measurand of interest is the sum of a boiling range to be defined. The definition of the boiling range, the extraction solvent, the clean-up inevitable to remove interfering components from the extracts, the selection of gas chromatography-flame ionisation detection (GC-FID) as the compulsory determination method and the calibration with an adequate TPH mixture is laid down in international standards [1-3]. Thus, TPH is a parameter necessarily to be defined by the method which has strictly to be followed through sample extraction, extract clean-up and instrumental analyte quantification.

The reference material BAM-U026 extend the range of matrix reference materials with certified TPH content. It is meant to be used for the verification of TPH quantification according to ISO 16703:2011 in soils [1] and closely related matrices such as sediments. EN 14039 [3] on the quantification of TPH in waste is technically identical to ISO 16703 regarding the instrumental TPH determination. Therefore, BAM-U26 may also serve to verify this standard procedure. The candidate material was prepared at BAM from "real-world" soils and characterised regarding homogeneity and stability of the TPH content. The certification of the mass fraction of TPH and its uncertainty followed the principles laid down in ISO 1703434 and ISO Guide 35 [7, 8]. Participating laboratories were invited on basis of their measurement capabilities proven in the proficiency testing scheme "Contaminated Sites" organised by BAM. Together with related reference materials BAM-U022 (sediment) and BAM-U021a (soil) the new material BAM-U026 covers the TPH range between 1000 mg/kg and 10000 mg/kg soil or sediment laid down as the recommended working range in ISO 16703:2011 [1].

## 2. Production of the candidate material

### 2.1 Selection of the starting material

A TPH contaminated sandy loamy soil was obtained from a soil remediation plant in Berlin, Germany. TPH quantification of a test portion revealed a concentration range suitable for certification after appropriate blending with a TPH free sandy loamy soil from a forest on BAM's test area Horstwalde near Berlin, Germany.

### 2.2 Preparation of the candidate material

The starting materials were air-dried and allowed to rest for several months at room temperature. Thereafter, they were separately submitted to classification by means of an automatic sieving station to yield fractions with an upper particle size of 125 µm. 19.20 kg of the contaminated soil obtained from Berlin and 16.87 kg of the TPH free soil were blended to arrive at the target TPH content near 1400 mg/kg. The combined material was homogenised using a 120 L stainless steel barrel equipped with a mixing insert inside of the barrel to accelerate and improve the mixing intensity. The barrel was rotated in a drum hoop mixer (J. Engelsmann AG, Ludwigshafen; Germany) for approx. 100 h. Further homogenisation and bottling were achieved using a Retsch spinning riffler and a well-established procedure of partitioning and back-mixing ("cross-riffling"). A batch of 512 units in 100 mL amber glass bottles containing  $(70.3 \pm 0.3)$  g of the material and sealed with screw caps with Teflon inserts was produced and numbered in the order of leaving the bottling process. The whole batch was stored at - 20 °C directly after bottling.

## 2.3 Analytical method

The determination of mineral oils in environmental matrices faces always the problem of complex and varying hydrocarbon mixtures that cannot be separated with reasonable effort and of lacking suitable reference substances for a large number of isomers and homologues. On the other hand, TPH can be quantified by GC-FID as a sum parameter since the flame ionisation detector yields signals proportional to the actual amount of C and H regardless of the hydrocarbon isomerism. Thus, TPH is a typical example for a measurand defined by the method, in this case as laid down in ISO 16703:2011. This definition includes the clean-up of extracts in order to remove interfering substances from the TPH mixture, the mandatory use of GC-FID and the prescription of the range of integration by the retention time markers n-decane (C10) and tetracontane (C40). The fraction of TPH between C10 and C40 is considered as total petroleum hydrocarbons (TPH) to be quantified according to this standard. Consequently, the gas chromatograph should be calibrated with an appropriate hydrocarbon mixture that mirrors the condition encountered in practise. In this study the calibration standard BAM-K010g was used. For the measurements on the candidate material a BPX-5 capillary column (15 m x 0.32 mm x 1 µm) and the following instrumental conditions were employed (Table 1).

Table 1: Instrumental conditions used for homogeneity and stability testing

Oven program	Example for a set of calibration solutions	
60 °C (5 min) → 360 °C (10 min)	cal 1: 0.1221 mg/mL	cal 6: 2.3179 mg/mL
Heating rate: 40 °C/min	cal 2: 0.2315 mg/mL	cal 7: 3.4312 mg/mL
Injection volume: 2.5 µL	cal 3: 0.5839 mg/mL	cal 8: 4.6140 mg/mL
Detector temperature: 370 °C	cal 4: 1.0560 mg/mL	cal 9: 6.9571 mg/mL
	cal 5: 1.6870 mg/mL	

## 2.4 Characterisation of the matrix and the TPH composition

Table 2 comprises the chemical characterisation of the matrix of the candidate material. The water content is at equilibrium with the atmosphere under typical laboratory conditions and corresponds to the relatively high content of organic carbon.

Table 2: Matrix characterisation of BAM-U026

Parameter	Value	Method
Particle size range in µm	< 125	Sieving
Water content in %	1.40 ± 0.02	Karl-Fischer-Titration
CHN-content in %	C: 2.17 ± 0.05; H: 0.41 ± 0.01; N: 0.10 ± 0.01	Elemental analysis

Figure 1 depicts the chromatogram of a typical extract of the candidate material obtained with the analytical procedure mentioned in 2.3 and outlined in ANNEX B. The mineral oil pattern in this soil is typical for an aged TPH contamination. A characteristic feature is the scarceness of n-alkanes (represented by clearly distinguished peaks on the TPH hump) being typical for aged diesel (gas oil) contaminations. This is in accordance with the fact that the TPH containing fraction of the material has rested for several years at ambient temperature.

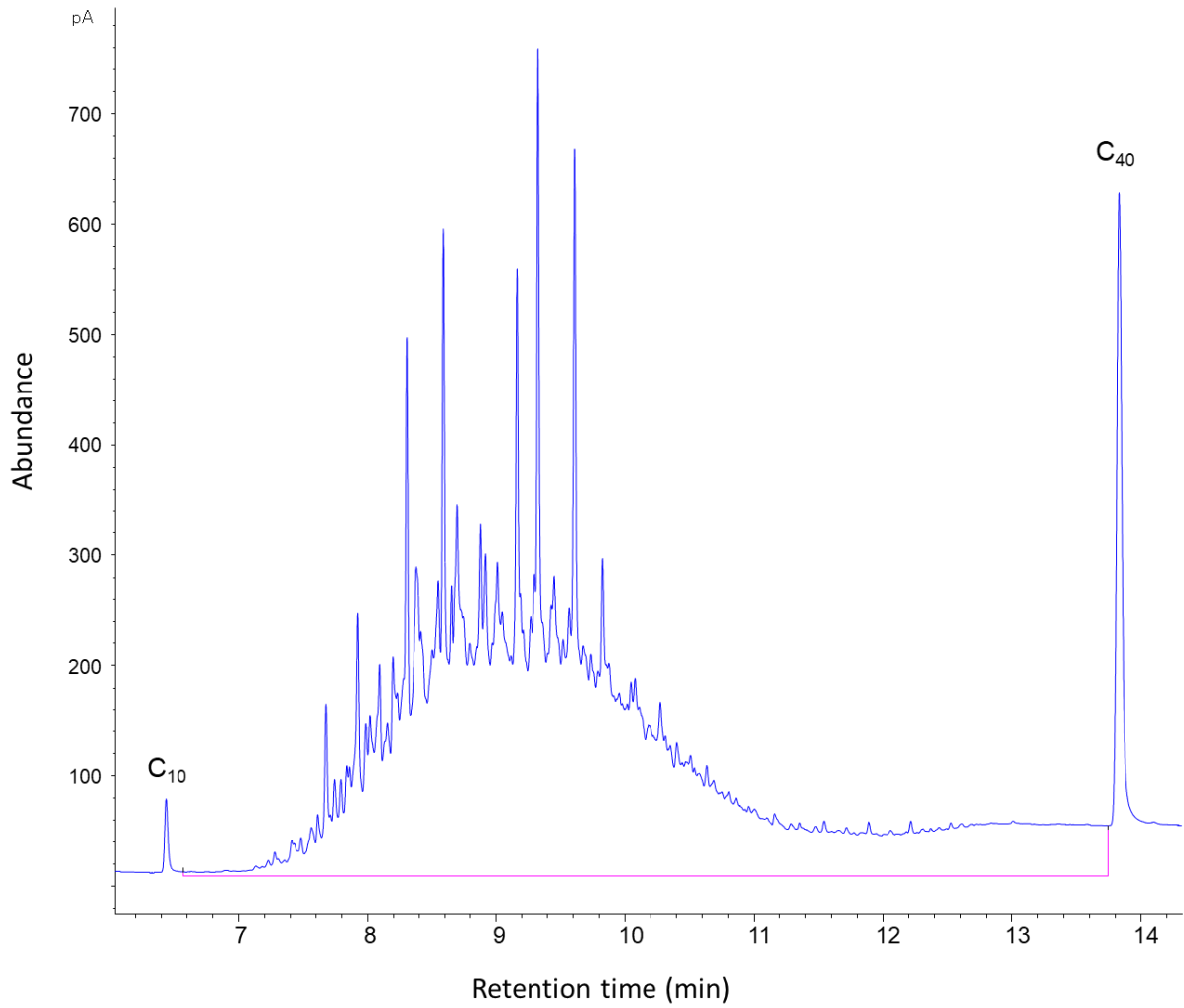


Fig. 1: Chromatogram of an extract of BAM-U026 according to ISO 16703:2011 (GC-FID).

Figure 2 (overleaf) displays for comparison a chromatogram for the calibrant BAM-K010g which is composed of diesel oil and lubricating base oil (1:1).

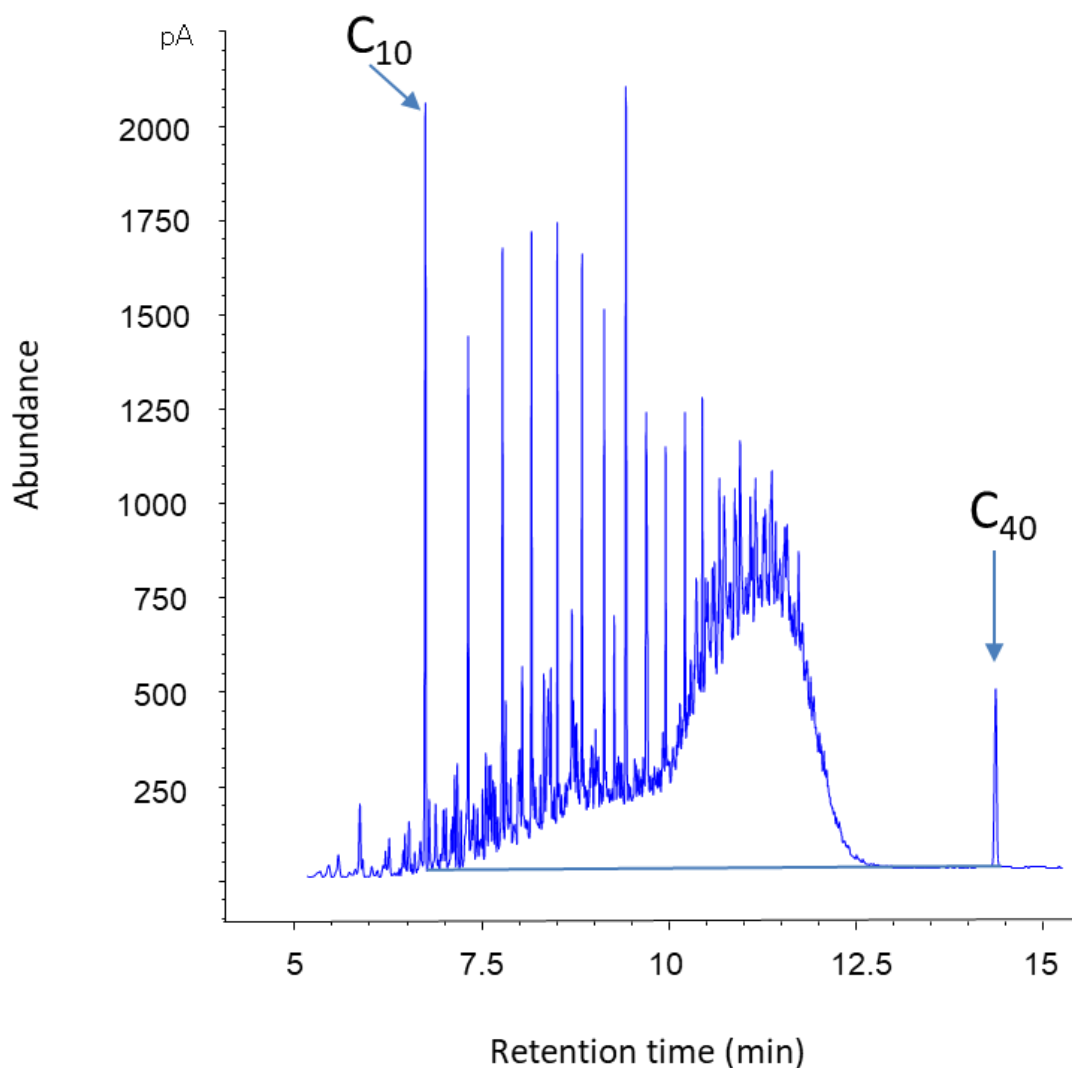


Fig. 2: Chromatogram of the calibration standard BAM-K010g (GC-FID)

## 2.5 Minimum sample intake

The minimum sample intake for one determination should be chosen in a way that no significant heterogeneity within the bottle is to be expected. Many years of experience with this matrix/analyte combination suggest a sample intake of 5 g for a single determination. This intake is also in accordance with the intake range recommended in ISO 16703:2011.

## 3 Homogeneity study

Eighteen units were selected equidistantly from the order of bottling of the whole batch of 512 bottles. They were analysed three times each according to ISO 16703:2011 using a sample intake of 5 g. The extraction procedure and instrumental parameters are given in ANNEX B and clause 2.3. The whole set of eighteen bottles was extracted once on each of three consecutive days. Processed extracts were analysed by GC-FID under repeatability conditions such that all 54 extracts were quantified against one calibration. Means and standard deviations are summarised in Figure 3. For the measurement data and the analysis of variance see ANNEX A. No evidence suggesting a rejection of the hypothesis that the material is sufficiently homogeneous was observed. The mean of the homogeneity study was 1371.6 mg/kg and the uncertainty of the TPH content between the bottles  $u_{bb}$  was estimated to be 24.96 mg/kg or expressed in relative terms  $u_{bb,r}$  to be 0.01820.

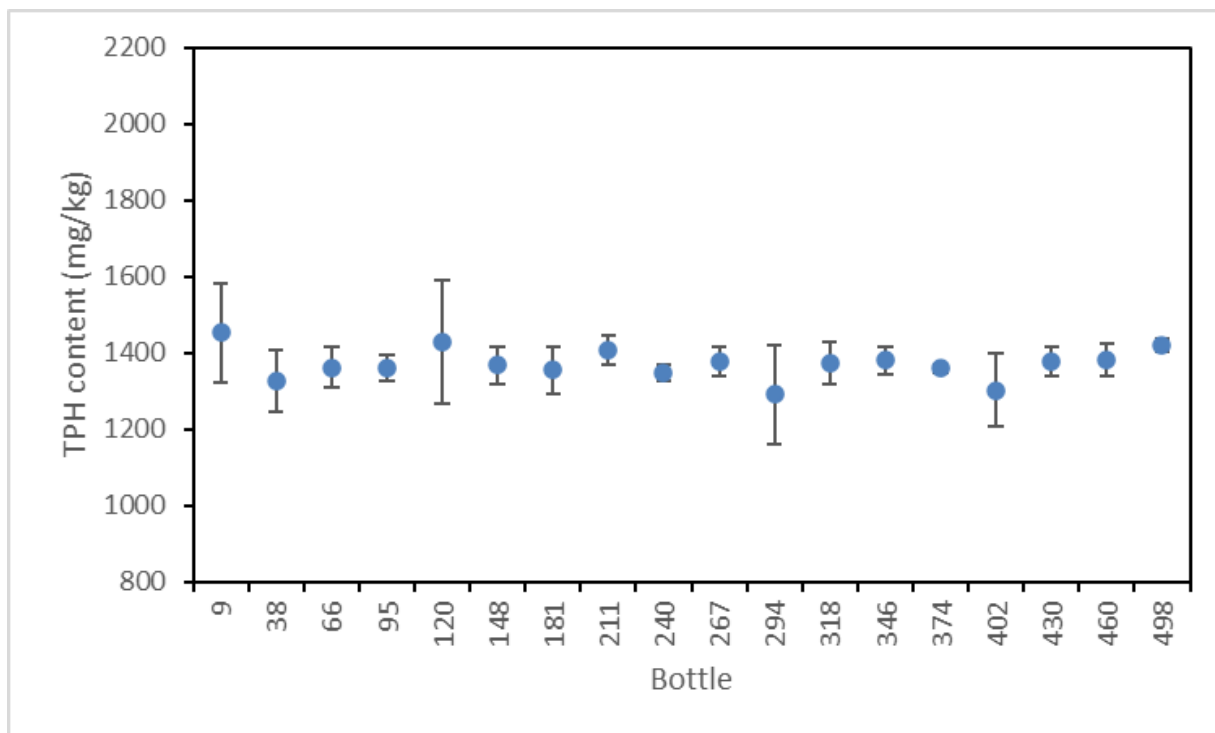


Fig. 3: Homogeneity study on selected bottles using GC-FID (means and standard deviations n = 3).

## 4 Stability study

### 4.1 Initial stability study

From earlier experience with organics [9] in various matrices a temperature-driven deterioration of the TPH content was to be expected also for this material. Selected units of the candidate material were submitted to a so-called isochronous [10] accelerated ageing at temperatures between +4 and +60 °C over periods of 1 - 12 months as shown in Table 3. After the respective periods of time the individual units were stored at -20 °C. All units were analysed for TPH in triplicate using the method described above and in ANNEX B under repeatability conditions after six months and after 12 months together with reference samples which had been kept at -20 °C and -80 °C since bottling. For the individual measurement data see ANNEX A.

Table 3: Accelerated ageing of selected units of BAM-U026: exposition temperatures, periods and number of exposed units.

Ageing time [Months]	+4 °C	+20 °C	+40 °C	+60 °C	Remark
1			2	2	<i>initial study</i>
3	2	2	2	2	<i>initial study</i>
6	2	2	2	2	<i>initial study</i>
10	2	2	2	2	<i>initial study</i>
12	2	2	2		<i>initial study</i>
24	2	2			<i>post certification monitoring</i>
36	2	2			<i>post certification monitoring</i>

The dependence of the thermal degradation on time is expected to be exponential. A non-negligible trend is obviously observed for the higher degradation temperatures. In order to obtain estimates for the thermal behaviour of the samples at the lower and especially at the storage temperature, a simple



Arrhenius model is assumed for the dependence of the reaction rate  $k(T)$  on temperature. A plot of the reaction rate  $k(T)$  over the inverse temperature is given in Figure 4.

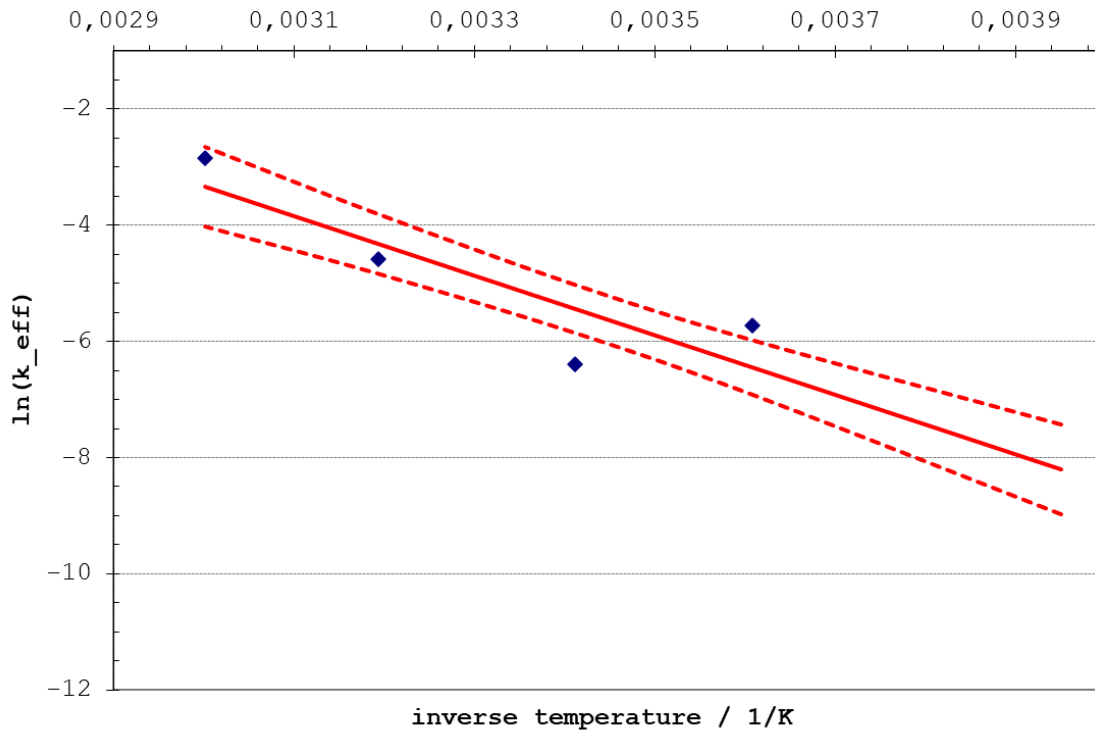


Fig. 4: Dependence of the degradation rate  $\ln(k_{\text{eff}})$  of TPH in BAM-U026 on the inverse temperature (semilogarithmic plot)

As can be seen from the plot, the temperature dependence can indeed be approximated by a straight line as a worst-case approximation. The corresponding confidence interval for the line is also given in the figure. By using these data and the assumed model, an estimate can be obtained when degradation will presumably force the mineral oil content to fall below the certified lower expanded uncertainty limit. In the sense of a worst-case estimation, these calculations are carried out for the reaction rates at the upper confidence limit of the line as shown in Figure 4. The times after which the TPH content falls short of  $U$  are given in Table 4.

Table 4: Estimation of shelf life

T [°C]	Months	Years
-20	157.1	13.8
4	37.5	3.2
20	14.6	1.2
40	4.4	0.4
60	1.4	0.1

Although the initial shelf life estimate for the storage temperature of -20 °C is quite considerable, longer exposure to room or even higher temperatures may drastically reduce the time of validity of BAM-U026. Therefore, a unique shelf life of one year after delivery from storage is established. Transportation/delivery time should be kept at the possible minimum and any exposure to heat should be avoided.

#### 4.2 Post-certification stability monitoring

The first rough estimation of stability will be updated by further measurements of units stored at -20 °C, 4 °C and 20 °C over the period of availability of the material. The post-certification measurements will be conducted according to the information given in Table 3.

## 5 Certification study

### 5.1 Strategy

The certification measurements were performed at BAM using four bottles of the candidate material. Two different operators extracted three subsamples (5 g) from two bottles (no. 270 and 271 or no. 413 and 414, respectively) according to ISO 16703 and treated the extracts further according to this standard. All extracts were analysed against separately prepared calibrations on three different GC-FID systems.

### 5.2 Evaluation of results and certified values

#### 5.2.1 Laboratory results

All three gas chromatographs (GC) were run with the conditions given in clause 2.3. GC1 used on-column injection and helium as carrier gas, GC2 was equipped with a cold-injection system and run with hydrogen as carrier gas. GC3 was run with on-column injection and hydrogen as carrier gas.

The results obtained are collected in Table 5 and Figure 5. Scrutiny of the laboratory protocols did not reveal any obvious technical reasons to exclude specific data from the evaluation of the certified value.

Table 5: Data sets obtained during in the certification study of BAM-U026

GC/Operator	Bottles	Replicate					
		1	2	3	4	5	6
GC1, Op1	270, 271	1492	1441	1453	1449	1408	1490
GC1, Op2	413, 414	1318	1404	1400	1394	1381	1426
GC2, Op1	270, 271	1484	1434	1493	1484	1424	1542
GC2, Op2	413, 414	1314	1382	1393	1374	1358	1415
GC3, Op1	270, 271	1424	1371	1380	1372	1318	1394
GC3, Op2	413, 414	1290	1324	1312	1335	1316	1356

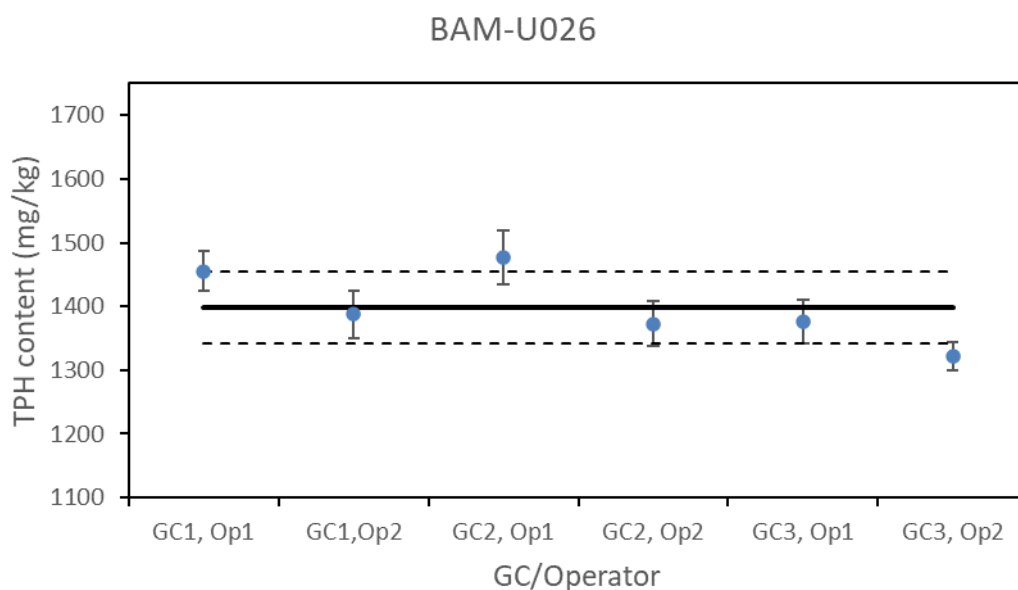


Fig. 5: Results of the certification study with mean of means. The solid and dashed lines represent the grand mean  $\pm$  standard deviation

The grand mean  $w_{\text{char}}$  of all data was 1398.5 mg/kg with a standard deviation SD of 57.50 mg/kg.

## 5.2.2 Traceability

As pointed out in Clause 2.3, the mineral oil content is a parameter defined by the method employed for its determination. The certified value is then the fraction of mineral oil obtained by the analytical procedure according to ISO 16703:2011 having been quantified in relation to the certified calibration standard BAM-K010g. Thus, the stated references for BAM-U026 are ISO 16703:2011 and the calibration standard BAM-K010g mentioned for this purpose therein.

## 5.2.3 Certified values and combined uncertainty

The estimate for the certified value  $w_{\text{cert}}$  is derived from  $w_{\text{char}}$  (mean of the certification study) after correction for the purity  $f_{\text{pur}}$  of the calibration standard BAM-K010g used in the homogeneity study and by the participants in the certification study according to Eq. (1):

$$w_{\text{cert}} = w_{\text{char}} * f_{\text{pur}} \quad (1)$$

According to Eq. 2 [11] the corresponding combined uncertainty  $u_{\text{com}}$  is composed of the uncertainty of characterisation  $u_{\text{char}}$ , the contribution due the inhomogeneity between bottles  $u_{\text{bb}}$ , the uncertainty due the purity  $u_{\text{pur}}$  of BAM-K010g and an additional allowance covering the uncertainty of handling by the user  $u_{\text{hand}}$ :

$$u_{\text{com},r}^2 = u_{\text{char},r}^2 + u_{\text{bb},r}^2 + u_{\text{pur},r}^2 + u_{\text{hand},r}^2 \quad (2)$$

where the index  $r$  refers to the values relative to  $w_{\text{cert}}$ .  $w_{\text{char}}$  is taken from clause 5.2.1 and the purity and the corresponding uncertainty of BAM-K010g is taken from the certificate as  $f_{\text{pur}} = 0.969$  and  $u_{\text{pur}} = 0.0075$ ,  $u_{\text{pur},r}$  is therefore  $0.0075/0.969 = 0.007740$ .  $u_{\text{hand},r}$  is set to 4% which accounts for the within laboratory repeatability earlier observed for the employed analytical procedure. Table 6 comprises the evaluation of  $w_{\text{cert}}$  and the expanded uncertainty  $U$ .

Table 6: Evaluation of the certified value and its uncertainty

Item	Value	Unit	Remark	After rounding
$w_{\text{char}}$	1398.5	mg/kg	Clause 5.1.1	
$w_{\text{cert}}$	1355.2	mg/kg	Eq. 1	1355
SD	55.7163	mg/kg	Clause 5.1.1	
$u_{\text{char}}$	22.7461	mg/kg	$SD/n^{1/2}$ , $n = 6$	
$u_{\text{char},r}$	0.01678	%		
$u_{\text{bb}}$	24.6644	mg/kg	$u_{\text{bb},r} \cdot w_{\text{cert}}$	
$u_{\text{bb},r}$	0.01820	%	Clause 3	
$u_{\text{pur}}$	10.4890	mg/kg	BAM-K010g certificate	
$u_{\text{pur},r}$	0.007740	%		
$u_{\text{hand}}$	54.2076	mg/kg	Clause 5.2.3	
$u_{\text{hand},r}$	0.04000	%		
$u_{\text{com}}$	64.6080	mg/kg	Eq. 2	
$u_{\text{com},r}$	0.04767	%		
$U$	129.2161	mg/kg	$k \cdot u_{\text{com},r}$ with $k = 2$	130
$U_r$	0.0956	%		

The certified value and the expanded uncertainty are rounded according to the recommendations of [1] and [12] and are given with respect to sample mass. The water content of  $(1.40 \pm 0.02)$  % remains stable if the material is handled according to the instructions in the certificate (see also Clause 6).

## **6 Information on the proper use of BAM-U026**

### **6.1 Shelf life**

From the stability study no shelf life decrease at -20 °C could be estimated. This is in agreement with early knowledge on the stability of TPH in soil at this temperature. A very conservative estimate for the stability at ambient temperature is six years from the date of certification. The validity of this estimate will be maintained by post-certification stability monitoring three years after certification. Thus, it will be assured that the certificate will be valid for at least 12 months beginning with the dispatch of the material from BAM.

### **6.2 Transport, storage and use**

The stability of the content of TPH allows dispatching the material at ambient temperature. On receiving, it is to be stored at -20 °C. Before withdrawing a subsample the bottle must have reached ambient temperature. Thereafter, the bottle must be closed tightly and stored at -20 °C again. The water content remains stable when the material is treated as described.

### **6.3 Safety instructions**

The soil was not sterilised, however, it is supposed to not exhibit any biological activity due to having been air-dried to constant mass and displaying a water content of 1.40 %. No hazardous effect is to be expected when the material is used under conditions usually adopted for the analysis of environmental matrices moderately contaminated with mineral oil hydrocarbons. Any unintended contact to this material should be treated as the contact to a dry soil without specifically hazardous properties.

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 References**

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## ANNEX A: Homogeneity and stability, measurement data

Results of the homogeneity study on BAM-U026. SD – Standard deviation.

Bottle No.	Replicate			Mean (mg/kg)	SD (mg/kg)
	1 (mg/kg)	2 (mg/kg)	3 (mg/kg)		
9	1238	1528	1393	1452.8	145.1
38	1236	1364	1384	1328.1	80.6
66	1321	1341	1422	1361.4	53.3
95	1333	1397	1351	1360.1	33.0
120	1309	1367	1615	1430.4	162.4
148	1352	1329	1424	1368.3	49.4
181	1336	1307	1424	1355.7	60.8
211	1413	1444	1369	1408.8	37.8
240	1325	1352	1366	1347.6	21.2
267	1358	1351	1421	1376.6	38.8
294	1301	1159	1418	1292.7	129.7
318	1312	1402	1408	1373.8	53.5
346	1353	1368	1423	1381.1	37.1
374	1358	1370	1350	1359.4	9.8
402	1338	1194	1375	1302.3	95.4
430	1339	1384	1412	1378.2	36.8
460	1374	1429	1347	1383.3	41.9
498	1405	1416	1440	1420.1	17.8

### ANOVA

Source of variability	Sum of Squares (SS)	Degrees of freedom (df)	Mean sum of Squares (MS)	F-value	P-value	critical F-value
between bottles	8470.,4	17	4982.67	0.62	0.845	1.925
within bottles	28547.,5	36	7929.98			
total	370185.0	53				

The grand mean of the homogeneity study is 1371.2 mg/kg. According to ISO Guide 35 the uncertainty between bottles  $u_{bb} = s_{bb}$  is estimated as the greatest result of eq. (1) and eq. (2). E. (1) yields no reasonable result and eq. (2) yields 24.96 mg/kg.

$$s_{bb} = \sqrt{\frac{(MS_{\text{among}} - MS_{\text{within}})}{n}} \quad (1)$$

$$s_{bb} = \sqrt{\frac{MS_{\text{within}}}{n}} \sqrt{\frac{2}{N(n-1)}} \quad (2)$$

where:  $n$  = Number of replicate determinations per sample  
 $N$  = Number of bottles analysed

The relative value  $u_{bb,r}$  is  $24.96/1371.2 = 0.01820$ .

Results of the stability study on BAM-U026.

Stability measurements (three replicates on each unit). results in mg/kg

Exposure	Unit	1.	2.	3.	Mean	SD	RSD (%)
Ref. -80°C	419	1404	1373	1314	1364	46	3.4
Ref. -20°C	421	1439	1401	1299	1380	72	5.2
Ref. -20°C	422	1302	1291	1317	1303	13	1.0
4 °C, 3 months	427	1320	1303	1352	1325	25	1.9
4 °C, 3 months	428	1394	1298	1397	1363	56	4.1
4 °C, 6 months	429	1390	1306	1343	1346	42	3.1
4 °C, 6 months	431	1368	1558	1390	1439	104	7.2
4 °C, 10 months	425	1314	1295	1340	1316	23	1.7
4 °C, 12 months	432	1292	1247	1314	1284	34	2.7
4 °C, 10 months	426	1285	1296	1368	1316	45	3.4
4 °C, 12 months	433	1323	1275	1286	1295	25	1.9
22 °C, 3 months	439	1336	1307	1296	1313	21	1.6
22 °C, 3 months	438	1312	1301	1321	1311	10	0.8
22 °C, 6 months	440	1299	1294	1271	1288	15	1.2
22 °C, 6 months	441	1293	1297	1288	1293	5	0.3
22 °C, 10 months	437	1313	1263	1293	1290	25	2.0
22 °C, 10 months	436	1299	1314	1328	1314	15	1.1
22 °C, 12 months	442	1248	1308	1309	1288	35	2.7
22 °C, 12 months	443	1273	1289	1240	1267	25	2.0
40 °C, 1 month	417	1335	1270	1260	1288	41	3.2
40 °C, 1 month	418	1302	1361	1263	1309	49	3.8
40 °C, 3 months	448	1291	1280	1236	1269	29	2.3
40 °C, 3 months	449	1327	1349	1253	1310	50	3.8
40 °C, 6 months	450	1239	1288	1197	1241	46	3.7
40 °C, 6 months	451	1239	1230	1277	1249	25	2.0
40 °C, 10 months	446	1298	1210	1304	1271	53	4.1
40 °C, 10 months	447	1212	1191	1165	1189	24	2.0

SD: standard deviation

RSD: relative standard deviation

Stability measurements (three replicates on each unit) after 12 months. results in mg/kg

Exposure	Unit	1.	2.	3.	Mean	SD	RSD (%)
40 °C, 12 months	452	1245	1133	1130	1169	66	5.6
40 °C, 12 months	453	1124	1116	1155	1132	21	1.8
60 °C, 1 month	415	1408	1189	1147	1248	140	11.2
60 °C, 1 month	416	1216	1205	1202	1208	7	0.6
60 °C, 3 months	456	993	1079	1010	1027	46	4.4
60 °C, 3 months	457	987	972	1029	996	30	3.0
60 °C, 6 months	458	871	874	906	884	19	2.2
60 °C, 6 months	459	1005	987	946	979	30	3.1
60 °C, 10 months	454	711	724	713	716	7	1.0

SD: standard deviation

RSD: relative standard deviation



## ANNEX B: Outline of the analytical procedure used for homogeneity and stability studies

