

BAM-U021a
Mineral oil contaminated soil
Certification Report

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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-U021a replaces sold-out BAM-U021 that displayed similar matrix and 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-U21a 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 Guides 34 and 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-U015b (sediment) and BAM-U022 (sediment), reference material BAM-U021a 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

Soil was obtained from a contaminated site under remediation in Bremen, Germany. TPH quantification of a test portion revealed a concentration range suitable for certification after appropriate blending with a TPH free soil. This was obtained from a forest on BAM’s test area Horstwalde near Berlin, Germany.

2.2 Preparation of the candidate material

The starting material from Horstwalde, a TPH free sandy loamy soil, was submitted to classification by means of an automatic sieving station to yield 39.2 kg of the fraction < 125 µm. After addition of 6.7 kg of a fraction < 63 µm from the soil obtained from Bremen a total of 45.9 kg was obtained displaying an appropriate TPH content. The 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 640 units in 100 mL amber glass bottles containing (71.1 ± 0.5) 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).

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-U021a

Parameter	Value	Method
Particle size range in µm	< 125	Sieving
Water content in %	1.68 ± 0.12	Drying loss at 105 °C
CHN-content in %	C: 4.06 ± 0.04; H: 0.59 ± 0.02; N: 0.19 ± 0.01	Combustion in

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 recent diesel (gas oil) contaminations. This is in accordance with the fact that the TPH containing fraction of the material has rested for about 15 years at room temperature.

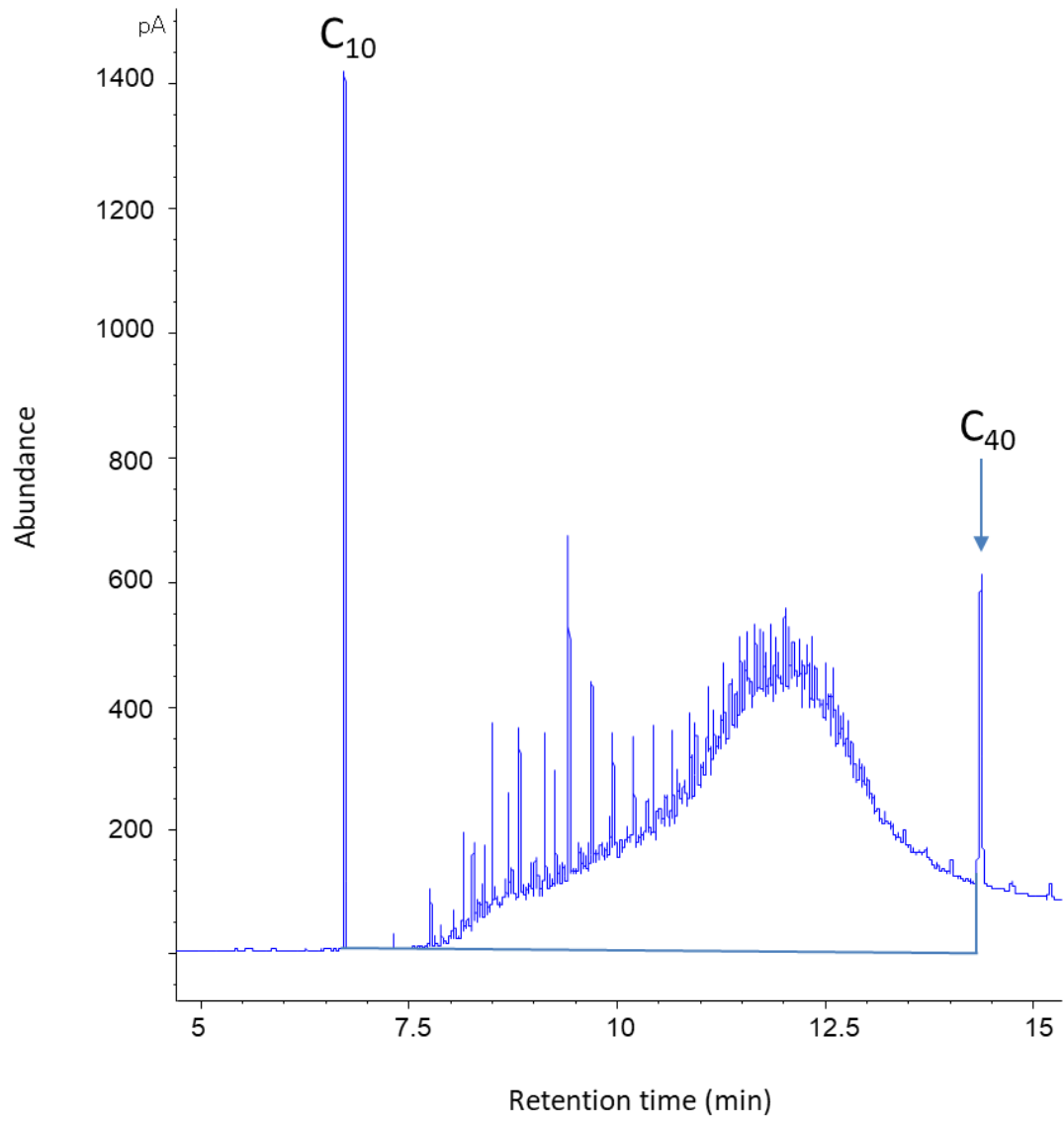


Fig. 1: Chromatogram of an extract of BAM-U021a according to ISO 16703:2011 (GC-FID).
Figure 2 (overleaf) displays for comparison a chromatogram for the calibrant BAM-K010g which is composed of diesel oil and lubricating base oil (1:1).

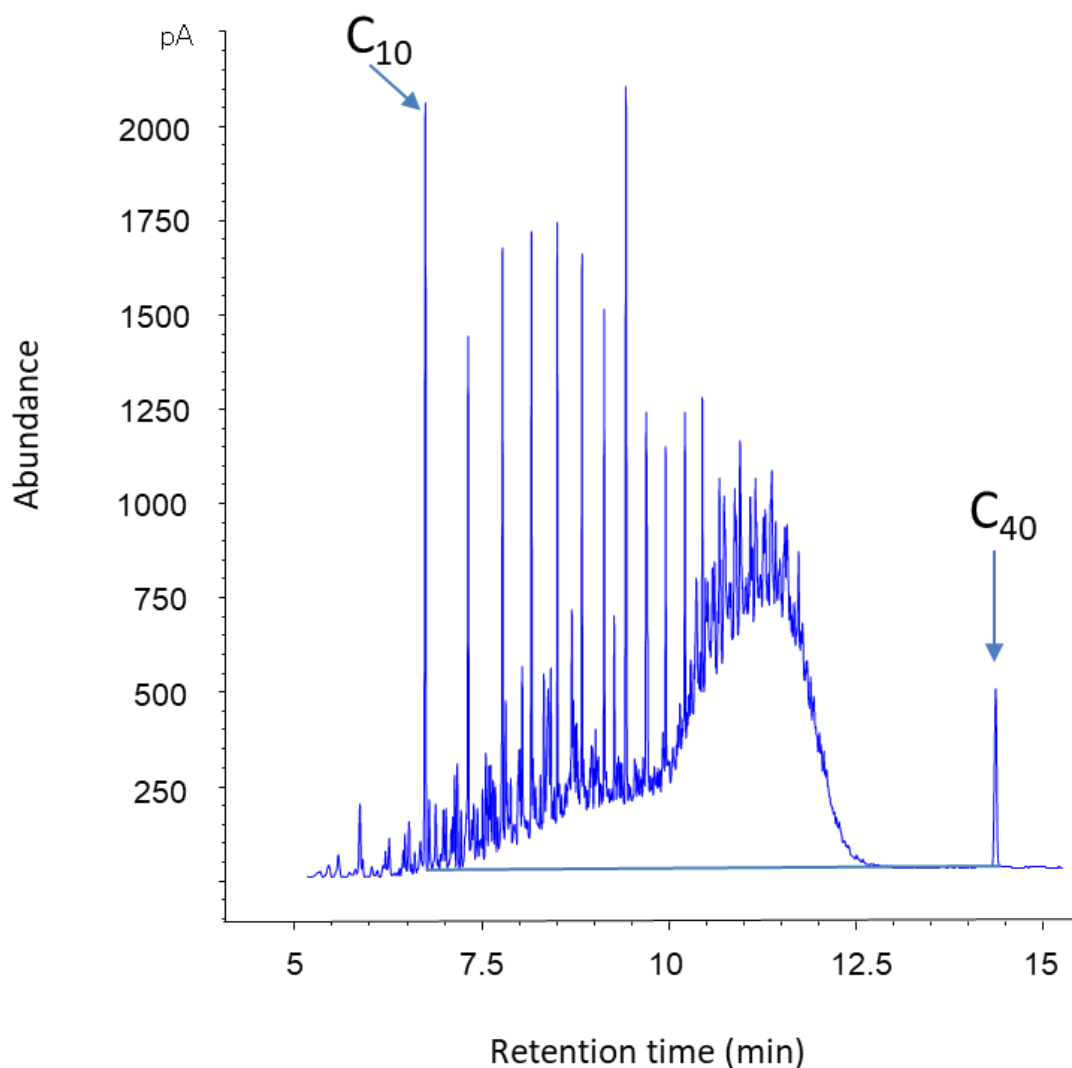


Fig. 2: Chromatogram of the calibration standard BAM-K010g (GC-FID)

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

Twenty units were selected equidistantly from the order of bottling of the whole batch of 640 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 20 bottles was extracted once on each of three consecutive days. Processed extracts were analysed by GC-FID under repeatability conditions such that all 60 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 2927.6 mg/kg and the uncertainty of the TPH content between the bottles u_{bb} was estimated as 55.04 mg/kg or expressed in relative terms as $u_{bb,r}$ as 0.01880.

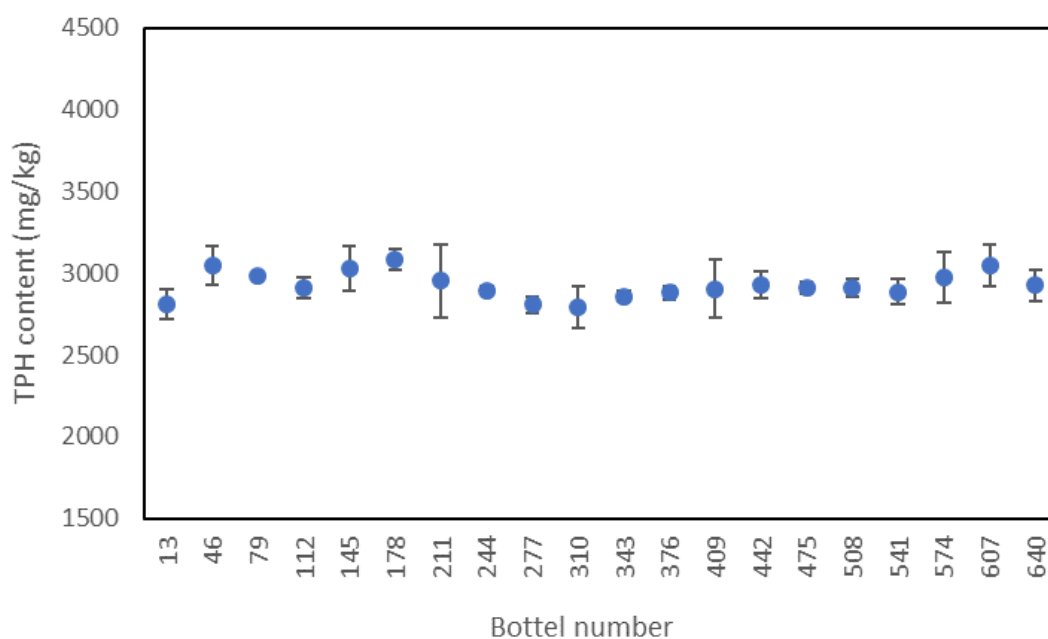


Fig. 3: Homogeneity study on selected bottles using GC-FID (means and standard deviations n = 3).

4 Stability study

From earlier experience with organics [10] 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 [9] 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-U021a: exposition temperatures, periods and number of exposed units.

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

In contrast to earlier soil and sediment reference materials (BAM-U015) but in accordance with BAM-U021 and BAM-U022 the reference material BAM-U021a did not display any significant decrease of the TPH content after accelerated ageing at ambient temperature and even at 40 °C and 60 °C within six months (Fig. 4). Only after 12 months at 60 °C a significant decrease of the TPH content was obvious. It is assumed that this is due to the storage of the starting materials in all three cases (BAM-U021,

BAM-U022, and BAM-U021a) over up to 15 years at ambient temperature since sampling. BAM-U015 in contrast had been prepared soon after sampling. It is assumed that the prolonged storage led to the degradation of the more instable TPH components.

Therefore, the usually applied simple Arrhenius model assuming a dependence of a detectable degradation reaction rate on the temperature [10] could not be used to arrive at an estimate for a significant loss of TPH with time. Although the shelf life at the storage temperature of -20 °C appears practically indefinite, any prolonged exposure to room and especially higher temperatures may nevertheless reduce the time of validity of BAM-U021a. Transportation/delivery time should be kept at the possible minimum and any exposure to elevated temperatures should be avoided. A post-certification monitoring will be scheduled with units stored at -80 °C, -20 °C, 4 °C and 20 °C five years after certification.

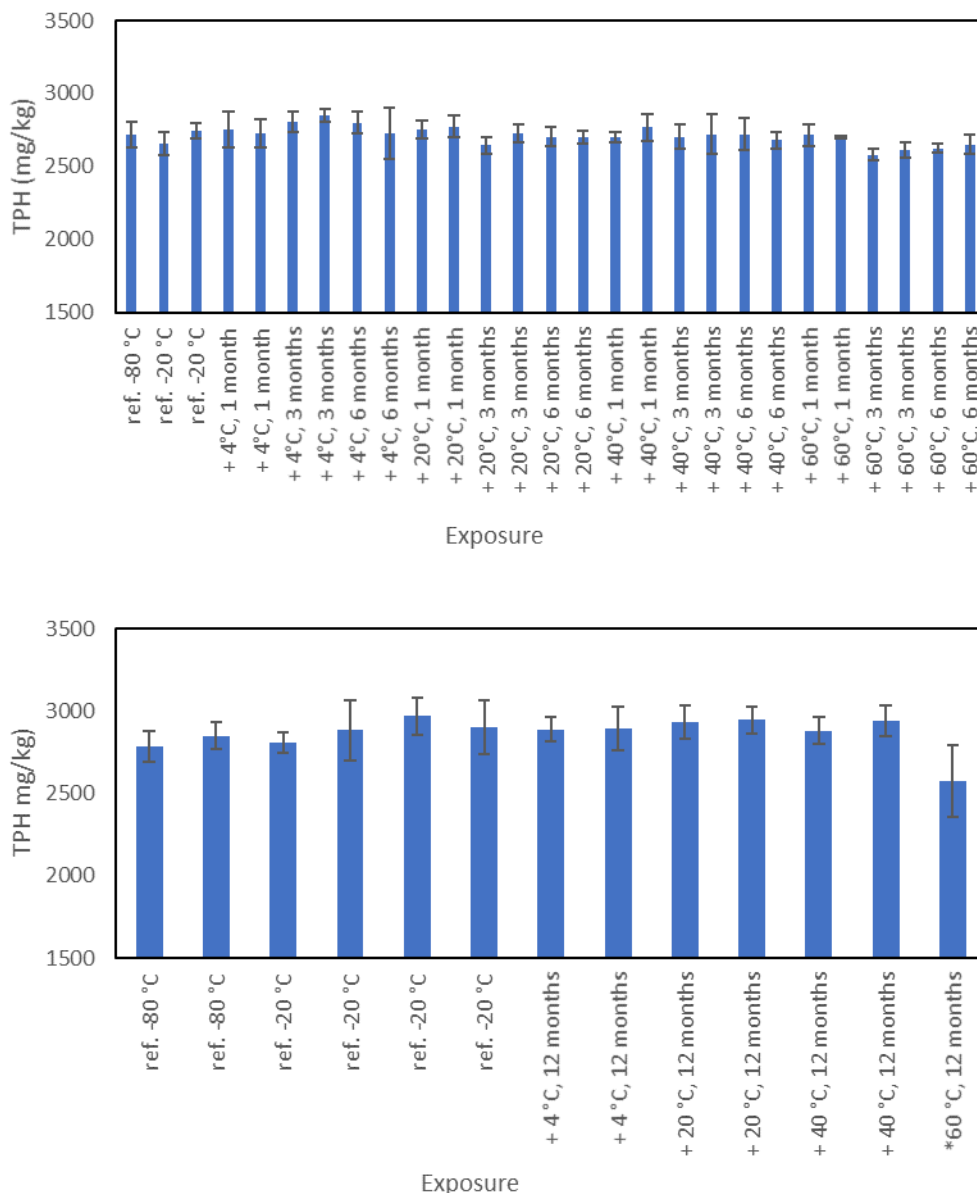


Fig. 4: Development of the TPH content in BAM-U021a after accelerated ageing for six (above) and 12 months using GC-FID (means and standard deviations n = 3).

5 Certification study

5.1 Selection of participating laboratories

A total of 11 laboratories were invited to participate in the certification exercise on grounds of their satisfactory performance in two recent proficiency testing rounds on TPH analysis in soil operated by BAM in 2018 and 2019. Some participants took also part in earlier certification studies on TPH in soil or sediment. Selection criteria included the consistency of documentation of extraction, clean-up, calibration and instrumental analysis according to ISO 16703:2011 and the declaration of commitment to comply with these requirements during the certification analyses. Additionally, the BAM laboratory responsible for candidate material production as well as homogeneity and stability measurements took part in this exercise. The participants are listed in alphabetical order in Table 4 (not identical with the numbering in the results Table 5).

Table 4: Participants in the certification exercise in alphabetical order

Analysen Service GmbH, Privates Institut für Umweltanalytik	Penzlin, Germany
Analysen Service GmbH, Umwelt- und Öllabor Leipzig	Leipzig, Germany
Bundesanstalt für Materialforschung und -prüfung (BAM) chemlab	Berlin, Germany
Bensheim, Germany	Bensheim, Germany
Eurofins Umwelt Ost GmbH	Bobritzsch, Germany
Landeskriminalamt Berlin	Berlin, Germany
Landeskriminalamt Brandenburg	Eberswalde, Germany
NIUTECH AG	Winterthur, Switzerland
SGS Institut Fresenius GmbH	Berlin, Germany
SYNLAB A&S Germany GmbH	Augsburg, Germany
WESSLING GmbH	Landsberg, Germany

Six replicate TPH determinations using an intake of 5 g of the candidate material were to be performed by each laboratory. For calibration, a sample of BAM-K010g was provided along with the candidate material. A questionnaire on the laboratory procedures had to be filled in. Results returned to BAM were scrutinised for consistency. No enquiries due to unclear or inconsistent data were necessary.

5.2 Evaluation of results and certified values

5.2.1 Treatment of laboratory results

The results of the certification study are collected in Table 5 and were evaluated in accordance with ISO Guide 35 [8]. A scrutiny of the laboratory protocols did not reveal any obvious technical reasons to exclude specific data from the evaluation of the certified value.

Although all participants in the intercomparison followed the same standardised procedure, significant differences caused by different implementations in different laboratories were to be expected. Thus, there was no good reason for assuming that the single values measured by the different laboratories would belong to a common mother distribution. This was confirmed by the statistical analysis within which the following statistical parameters were calculated using the software SoftCRM [11]:

- the mean of laboratory means w_{char} : 2890.4 mg/kg
- the standard deviation of the distribution of laboratory means s : 275.75 mg/kg
- the standard deviation of the mean of laboratory means (standard uncertainty u_{char}): 83.14 mg/kg

The following statistical tests were carried out (at significance levels α of 0.05 and 0.01):

- Cochran test for the identification of outliers with respect to laboratory variance
- Grubbs test for the identification of outliers with respect to the mean
- Dixon and Nalimov tests for the verification of possible outlier indications
- Kolmogorov-Smirnov test (Lilliefors version) for the normality test
- Tests for variance homogeneity, skewness and kurtosis

The main features are as follows:

- Scheffé test: Many laboratory data sets differ significantly if compared directly.
- Snedecor F test: Differences between laboratories are statistically significant ($\alpha = 0.05$).
- Bartlett test: Variances are not homogeneous ($\alpha = 0.05$).
- Cochran test: L10 and L08 are stragglers ($\alpha = 0.05$).
- Dixon test: No outliers detected.
- Nalimov test: L01 is an outlier ($\alpha = 0.01$).
- Grubbs test: L01 is a straggler ($\alpha = 0.05$).
- Kolmogorov-Smirnov-Lilliefors test: Laboratory means are normally distributed ($\alpha = 0.05$).
- Skewness & kurtosis test: Laboratory means are not normally distributed ($\alpha = 0.05$).

No data were removed from further evaluation on basis of the statistical tests. Therefore, the following data were used to arrive at the certified value and its uncertainty:

Mean of laboratory means w_{char} : 2890.35 mg/kg

Standard deviation SD of the laboratory means: 275.75 mg/kg

Standard uncertainty u_{char} of the laboratory means ($=\text{SD}/n^{1/2}$ with n = number laboratories): 83.14 mg/kg

Relative standard uncertainty $u_{\text{char,r}} = u_{\text{char}}/w_{\text{char}}$: 0.02876.

Table 5: Data sets received from the participants in the certification study of BAM-U021a

Laboratory	Replicate						mean	SD ^a
	# 1	# 2	# 3	# 4	# 5	# 6		
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
L01	3340	3408	3556	3520	3554	3676	3509	119.2
L02	2802	2976					2889	123.0
L03	3011.697	3119.257	3193.69	3233.35	3219.835	3045.021	3137.14	93.6
L04	2794	2706	2680	2773	2766	2753	2745	43.4
L05	2755.4	2761	2758.2	2754.6	2803.1	2760.7	2765.5	18.6
L06	2736.4	2560.9	2538	2623.4	2536.3	2569.8	2594.1	76.5
L07	2650	2670	2730	2610	2570	2610	2640	56.2
L08	2673.03	2708.373	2943.07	3153.56	2908.841	2649.996	2839.480	197.5
L09	3115.8	3080.2	3149.4	3091.9	3157.3	3078.2	3112.1	34.7
L10	2820	2700	2780	2720	2260	2420	2616.7	224.3
L11	2967	3035	2754	2891	2888	3138	2945.5	133.0

^a standard deviation

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-U021a 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_{cert} is derived from w_{char} (mean of the certification study) after correction for the purity f_{pur} of the calibration standard BAM-K010g used in the homogeneity study and by the participants in the certification study according to Eq. (1):

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

The corresponding combined uncertainty is composed of the uncertainty of characterisation $u_{char,r}$, the contribution due the inhomogeneity between bottles $u_{bb,r}$, and the uncertainty due the purity $u_{pur,r}$ of BAM-K010g according to Eq. 2 [12]:

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

where the index r refers to the relative uncertainties. w_{char} is taken from clause 5.2.1 and the purity and the corresponding uncertainty of BAM-K010g is taken from the certificate as $f_{pur} = 0.969$ and $u_{pur} = 0.0075$, $u_{pur,r}$ is therefore $0.0075/0.969 = 0.0077399$, $u_{char,r}$ is given in Clause 5.2.1 as 0.02876, and $u_{bb,r}$ in Clause 3 as 0.01880.

The certified value w_{cert} and its uncertainty u_{com} are given in Table 6. The expanded uncertainty $U = k u_{com}$ is obtained using a coverage factor k of 2. The certified value and the expanded uncertainty are rounded according to the recommendations of [1] and [13] and are given with respect to sample mass. The water content of (1.68 ± 0.12) % remains stable if the material is handled according to the instructions in the certificate (see also Clause 6).

Table 5: Certified TPH content of BAM-U021a in mg/kg

	Certified value w_{cert} , corrected for purity	Combined uncertainty u_{com} of the certified value	Expanded uncertainty U of the certified value
According to (1), (2)	2800.75	101.799	203.598
After rounding	2801	102	204

6 Information on the proper use of BAM-U021a

6.1 Shelf life

From the stability study no reasonable shelf life at -20 °C could be estimated as no decrease of the TPH content could be detected at temperatures up to 40 °C. A very conservative estimate for the stability is six years from the date of certification. The validity of this estimate will be maintained by post-certification stability monitoring five years after certification. Therefore, the certificate will be valid until then 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 1.68%. 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.

6.4 Legal notice

Neither the Bundesanstalt für Materialforschung und -prüfung (BAM) nor any person acting on their behalf make any warranty or representation, express or implied, that the use of any information, material, apparatus, method or process disclosed in this document may not infringe privately owned rights, or assume any liability with respect to the use of, or damages resulting from the use of any information, material, apparatus, method or process disclosed in this document.

7 References

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ANNEX A: Homogeneity and stability, measurement data

Results of the homogeneity study on BAM-U021a. SD – Standard deviation.

Bottle No.	Replicate			Mean (mg/kg)	SD (mg/kg)
	1 (mg/kg)	2 (mg/kg)	3 (mg/kg)		
13	2736	2909	2791	2812.0	88.4
46	3170	3039	2939	3049.3	115.8
79	2967	2989	2983	2979.7	11.4
112	2837	2951	2944	2910.7	63.9
145	2912	3179	3002	3031.0	135.8
178	3061	3035	3156	3084.0	63.7
211	2715	2982	3160	2952.3	224.0
244	2897	2916	2875	2896.0	20.5
277	2825	2848	2754	2809.0	49.0
310	2772	2927	2681	2793.3	124.4
343	2866	2821	2886	2857.7	33.3
376	2837	2891	2917	2881.7	40.8
409	2795	3108	2805	2902.7	177.9
442	2891	2876	3027	2931.3	83.2
475	2888	2890	2954	2910.7	37.5
508	2883	2974	2877	2911.3	54.4
541	2861	2975	2823	2886.3	79.1
574	2830	2965	3138	2977.7	154.4
607	3194	2945	3005	3048.0	129.9
640	2861	2995		2928.0	94.8

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	380789.13	19	20041.5332	1.83	0.0546	1.86
within bottles	427174.667	39	10953.1966			
total	807963.797	58				

The grand mean of the homogeneity study is 2927.6 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 55.04 mg/mg and eq. (2) yields 30.70 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 $55.04/2927.6 = 0.01880$.

Results of the stability study on BAM-U021a.

Stability measurements (three replicates on each unit) after 6 months, results in mg/kg

Exposure	Unit	1.	2.	3.	Mean	SD	RSD (%)
ref. -80 °C	391	2728	2627	2806	2720	90	3.3
ref. -20 °C	393	2564	2717	2692	2658	82	3.1
ref. -20 °C	394	2804	2708	2727	2746	51	1.9
+ 4°C, 1 month	399	2771	2617	2862	2750	124	4.5
+ 4°C, 1 month	400	2810	2623	2744	2726	95	3.5
+ 4°C, 3 months	401	2884	2767	2763	2805	69	2.5
+ 4°C, 3 months	402	2825	2825	2897	2849	42	1.5
+ 4°C, 6 months	403	2881	2784	2740	2802	72	2.6
+ 4°C, 6 months	404	2611	2633	2926	2723	176	6.5
+ 20°C, 1 month	408	2818	2698	2745	2754	60	2.2
+ 20°C, 1 month	410	2720	2857	2749	2775	72	2.6
+ 20°C, 3 months	411	2707	2600	2630	2646	55	2.1
+ 20°C, 3 months	412	2796	2679	2710	2728	61	2.2
+ 20°C, 6 months	413	2645	2693	2775	2704	66	2.4
+ 20°C, 6 months	415	2660	2747	2705	2704	44	1.6
+ 40°C, 1 month	419	2675	2693	2737	2702	32	1.2
+ 40°C, 1 month	420	2703	2728	2874	2768	92	3.3
+ 40°C, 3 months	627	2800	2671	2638	2703	86	3.2
+ 40°C, 3 months	628	2871	2603	2686	2720	137	5.0
+ 40°C, 6 months	421	2605	2736	2823	2721	110	4.0
+ 40°C, 6 months	422	2718	2618	2703	2680	54	2.0
+ 60°C, 1 month	423	2783	2640	2719	2714	72	2.6
+ 60°C, 1 month	398	2691	2696	2706	2698	8	0.3
+ 60°C, 3 months	632	2618	2542	2585	2582	38	1.5
+ 60°C, 3 months	633	2630	2657	2556	2614	52	2.0
+ 60°C, 6 months	424	2619	2658	2596	2624	31	1.2
+ 60°C, 6 months	425	2591	2718	2646	2652	64	2.4

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 (%)
ref. -80 °C	391	2691	2880	2776	2782	95	3,4
ref. -80 °C	392	2781	2937	2827	2848	80	2,8
ref. -20 °C	393	2737	2823	2861	2807	64	2,3
ref. -20 °C	394	2683	2925	3044	2884	184	6,4
ref. -20 °C	395	2837	3012	3053	2967	115	3,9
ref. -20 °C	396	2766	2862	3085	2904	164	5,6
+ 4 °C, 12 months	405	2832	2862	2972	2889	74	2,6
+ 4 °C, 12 months	406	2924	2745	3002	2890	132	4,6
+ 20 °C, 12 months	414	2939	2829	3032	2933	102	3,5
+ 20 °C, 12 months	416	2877	2920	3036	2944	82	2,8
+ 40 °C, 12 months	629	2868	2806	2967	2880	81	2,8
+ 40 °C, 12 months	630	2964	2835	3021	2940	95	3,2
*60 °C, 12 months	631	2728	2324	2668	2573	218	8,5

SD: standard deviation

RSD: relative standard deviation

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

