BAM-U021: Mineral oil Contaminated Soil

Certification Report

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1 Introduction

Mineral oils are among the most important organic pollutants in environmental compartments and have been in the centre of concern of international standardisation bodies 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] and certified reference materials for method verification [5].
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, gas chromatography-flame ionisation detection (GC/FID) as the compulsory determination method and the calibration with an adequate TPH mixture is laid down in the 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-U021 is meant to be used for the verification of the quantification of TPH according to ISO 16703:2005 in soils and closely related matrices such as sediments. The candidate material was prepared at BAM from a “real-world” soil and characterised with regard to 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 Guide 35 [6]. 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-U15b (sediment) and BAM-U022 (sediment), reference material BAM-U021 covers the TPH-range between 1000 and 10000 mg/kg soil or sediment laid down as the recommended working range in ISO 16703:2005.

2 Production of the candidate material

2.1 Selection of the starting material

The sandy soil was sampled from a heap of excavated contaminated soil at a facility concerned with remediation of contaminated sites (Umweltschutz Ost, Berlin, Germany). TPH quantification of a test portion revealed a concentration range suitable for certification.

2.2 Preparation of the candidate material

The wet starting material (approx. 280 kg) was air-dried to constant mass (270 kg) and submitted to classification by means of an automatic sieving station to yield 17.0 kg of the fraction < 125 µm. After addition of 3.6 kg of a fraction < 63 µm from an earlier sampling of a similar heap a total of 20.6 kg was obtained.
Then, 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 in a drum hoop mixer (J. Engelsmann AG, Ludwigshafen; Germany) for approx. 121 h. Further homogenisation and bottling was achieved using a Retsch spinning riffler and a well-established procedure of partitioning and back-mixing (“cross-riffling”). A batch of 320 units were bottled in 100 mL amber glass bottles containing (62.7 ± 0.3) g of the material sealed with screw caps with Teflon inserts 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 not to be separated with reasonable effort and 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 16703:2005. This definition includes the clean-up of extracts in order to remove interfering substances from the TPH mixture, the use of GC/FID and the prescription of the range of integration by the retention time markers n-decane (C_{10}) and tetracontane (C_{40}). The fraction of TPH between C_{10} and C_{40} is considered as mineral oil of 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-K010[1] 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.

Oven program
60 °C (5 min) → 360 °C (5 min)
Heating rate: 40 °C/min
Injection volume: 3 µL
Detector temperature: 370 °C

Example for a set of calibration solutions			
cal 1:	0.5113 mg/mL	cal 5:	2.0327 mg/mL
cal 2:	0.7761 mg/mL	cal 6:	2.5710 mg/mL
cal 3:	1.0237 mg/mL	cal 7:	3.0595 mg/mL
cal 4:	1.5056 mg/mL	cal 8:	4.0783 mg/mL

2.4 Characterisation of the matrix and the TPH composition

Table 1 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 1: Matrix characterisation of BAM-U021

Measurand	**Value**	**Method**
Particle size range (µm)	0 – 125	Sieving
Water content[a] (%)	0.350 ± 0.004	*Karl-Fischer*-Titration
Loss on drying[a] (%)	0.60 ± 0.10	Gravimetry after drying to constant mass at 105 °C (DIN ISO 11465)

[a] means and standard deviations (n = 9)

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 sediment is typical for this type of matrix with an aged TPH contamination. A characteristic feature is the scarceness of n-alkanes (represented by clearly distinguished peaks on the TPH hump) as being typical for recent diesel (gas oil) contaminations. The two distinct peaks between 9 and 10 min are probably pristane and phytane, typical mineral oil components which tend resist degradation in the environment.

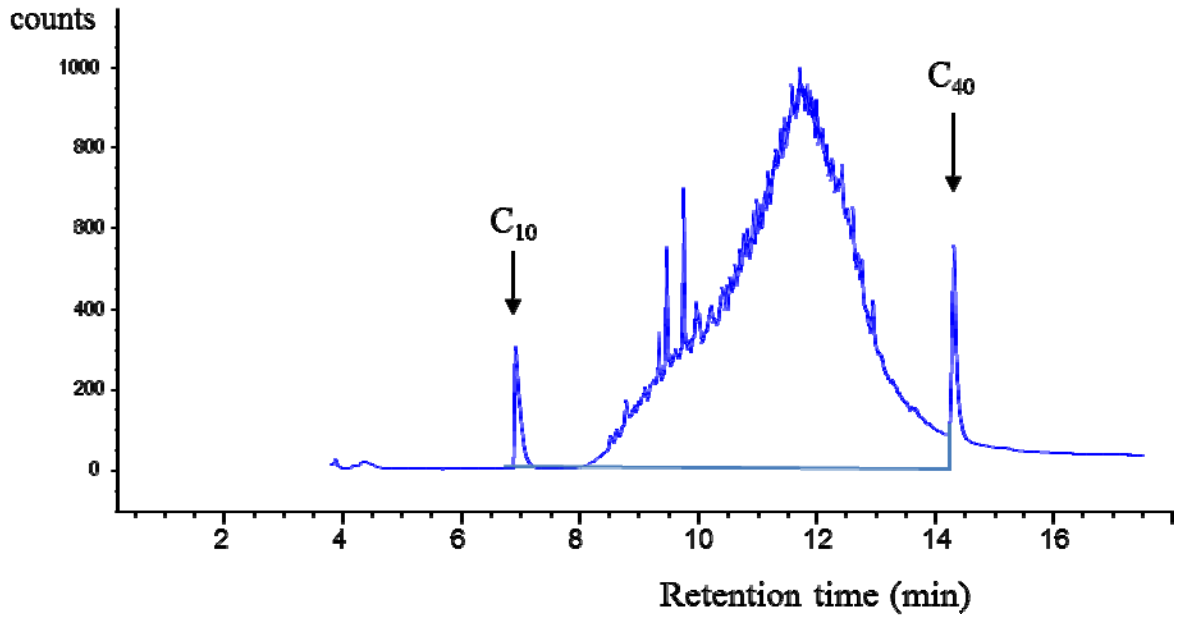

Fig. 1: Chromatogram of an extract of BAM-U021 according to ISO 16703:2005 (GC/FID)

[1] Certified calibration standard BAM-K010 is mentioned for this purpose in ISO 16703:2005 and available from BAM: www.webshop.bam.de

Figure 2 displays for comparison a chromatogram for the calibrant BAM-K010 which is composed of diesel oil and lubricating base oil (1:1).

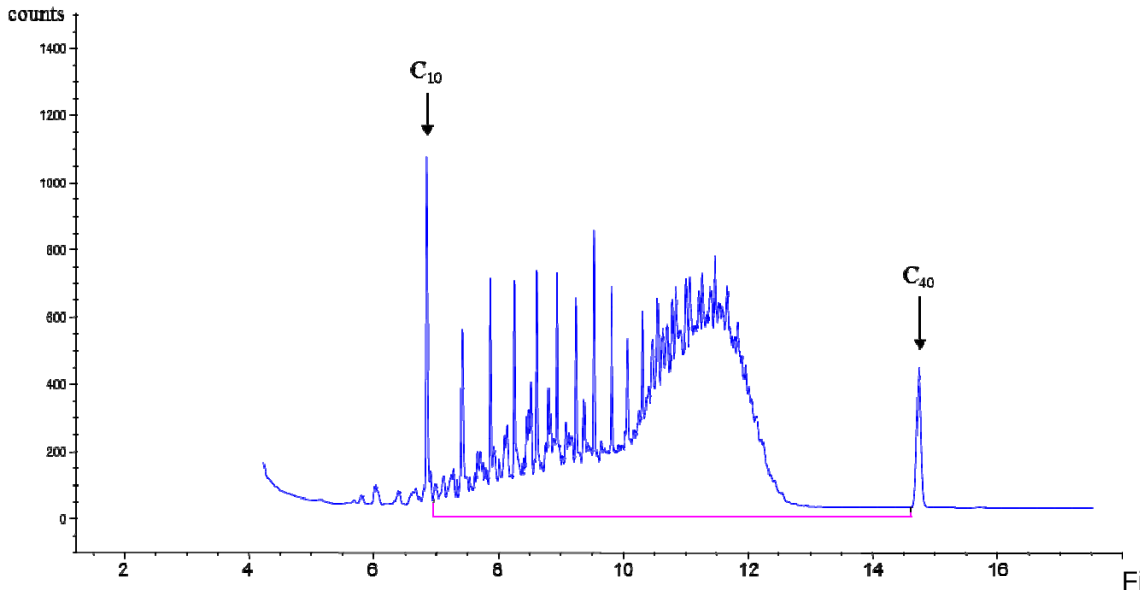

Fig. 2: Chromatogram of the calibration standard BAM-K010 (GC/FID)

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 16703:2005.

3 Homogeneity study

Fifteen units were selected equidistantly from the order of bottling of the whole batch of 320 bottles. They were analysed three times each according to ISO 16703:2005 using a sample intake of 5 g. The extraction procedure and instrumental parameters are given in ANNEX B. The whole set of 15 bottles was extracted once on each of three consecutive days. Processed extracts were analysed by GC/FID using the method given in clause 2.3 under repeatability conditions such that all 45 extracts were quantified against one calibration after randomisation. 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 3041 mg/kg and the uncertainty of the TPH content between the bottles u_{bb} was estimated as 30.53 mg/kg or expressed in relative terms as $u_{bb,r}$ of 0.010039461.
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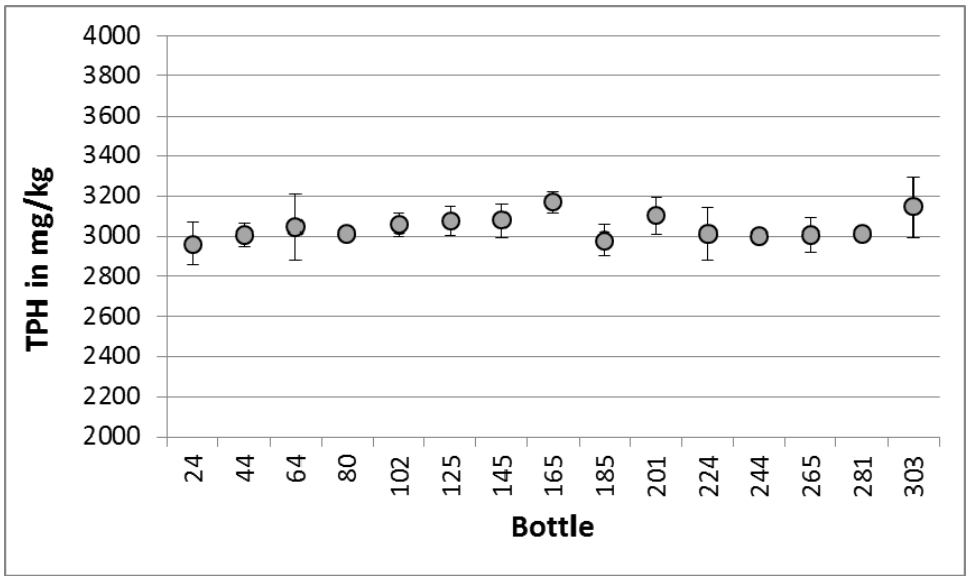


Fig. 3: Results of the homogeneity study (GC/FID, n = 3).

4 Stability study

From experience [5] a temperature-driven deterioration of the TPH content was to be expected also for this material. In the initial stability study thirteen units of the candidate material were submitted to an isochronous [7] accelerated ageing at temperatures between 4 °C and 60 °C over periods between 1 month and 6 months as shown in Table 2. 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 together with a reference sample which had been kept at –20 °C since bottling. For the individual data see ANNEX A.

Table 2: Accelerated ageing of exposed samples[1)]

Ageing [Months]	+4 °C	+20 °C	+40 °C	+60 °C	Remark
1	53	62	73	77	initial study
3	54	63	74	78	initial study
6	55	65	75	79	initial study
12	56	66	76	-	2)
24	57	67	-	-	2)
36	58	68	-	-	2)
48	59	69	-	-	2)
60	60	70	-	-	2)

[1)] Bottle numbers
[2)] post certification monitoring

In contrast to earlier soil and sediment reference materials BAM-U021 did not display any significant decrease of the TPH content after accelerated ageing at 40 °C and 60 °C (Fig. 4).

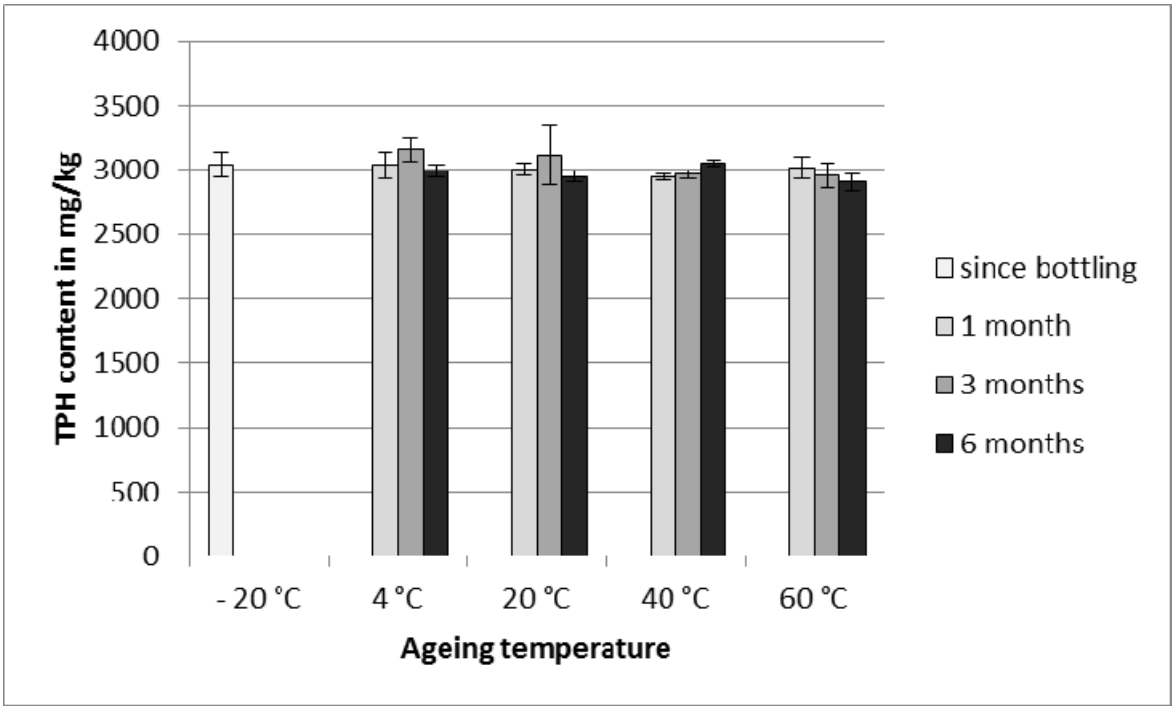


Fig. 4: Development of the TPH content in BAM-U021 after accelerated ageing (GC-FID, n=3).

Therefore, the usually applied simple *Arrhenius* model assuming a dependence of the degradation reaction rate on temperature did not produce any reasonable estimates for the loss of TPH with time. This may be due to the fact that this specific material originated from an excavation heap being submitted to biological TPH remediation. Possibly, the TPH fraction susceptible to degradation has been removed leaving the more stable TPH components.
Although the shelf life at a storage temperature of -20 °C is practically indefinite, any exposure to room or even higher temperatures may nevertheless reduce the time of validity of BAM-U021. Therefore, a unique shelf life of **two years after delivery from storage** is established. Transportation/delivery time should be kept at the possible minimum and any exposure to heat should be avoided.
The first rough estimation of stability will be updated by further measurements of units stored at 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 2.

5 Certification study

5.1 Selection of participating laboratories

A total of 13 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. 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 16703:2005 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 3 (not identical with the numbering in the data table 4).

Table 3: Participating laboratories

ALBO-tec – Technologiezentrum für Analytik und Bodenmechanik	D-45473	Mülheim/Ruhr
Analytik Institut Dr. Rietzler & Kunze GmbH & Co. KG	D-09599	Freiberg
BAM Bundesanstalt für Materialforschung und -prüfung, FB 1.2	D-12489	Berlin
Chemisches Labor Dr. Wirts + Partner	D-30559	Hannover
Deutsche Bahn AG	D-14774	Brandenburg
Eurofins Umwelt Ost GmbH	D-09633	Halsbrücke
GDF SUEZ E&P DEUTSCHLAND GMBH	D-29410	Salzwedel
ICA - Institut für Chemische Analytik GmbH	D-04229	Leipzig
PWU Potsdamer Wasser- und Umweltlabor GmbH & Co. KG	D-14473	Potsdam
Südsachsen Wasser GmbH	D-09125	Chemnitz
UCL Umwelt Control Labor GmbH	D-24111	Kiel
Umweltlabor der Stadtentwässerung Schweinfurt	D-97424	Schweinfurt
WESSLING Laboratorien GmbH	D-30625	Hannover

Six replicate TPH determinations using an intake of 5 g of the candidate material were to be performed by each laboratory. 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 4 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.

Table 4: Data sets received from the participants in the certification study of BAM-U021

Laboratory	**Replicate**								
	# 1	**# 2**	**# 3**	**# 4**	**# 5**	**# 6**	**mean**	**s**[a]	**s_{rel}**[b]
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**%**
L01	3390	3436	3297	3330	3301	3356	3352	54.1	1.6
L02	3360	3220	2830	2800	2960	2980	3025	221.4	7.3
L03	3996	3956	3788	3816	3948	3720	3871	110.9	2.9
L04	3180	3480	3260	3300	3420	3430	3345	116.2	3.5
L05	3275	3373	3223	3271	3309	3399	3308	66.6	2.0
L06	3877	3753	3761	3789	3642	3675	3750	83.7	2.2
L07	3980	3980	3880	3920	3780	3880	3903	75.3	1.9
L08	3146	3089	2991	2931	3378	3325	3143	178.5	5.7
L09	3320	3160	3320	3310	3310	3480	3317	101.3	3.1
L10	4047	4176	4175	4272	4030	4046	4124	98.0	2.4
L11	4604	4423	4497	4639	4506	4235	4484	144.8	3.2
L12	3548	3546	3377	3720	3494	3563	3541	111.1	3.1
L13	3015	2963	3077	3170	3009	3004	3040	73.6	2.4

[a] standard deviation
[b] relative standard deviation

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 computer software SoftCRM [9]:

- the mean of laboratory means w_{char}: 3554 mg/kg
- the standard deviation of the distribution of laboratory means s: 443.96 mg/kg
- the standard deviation of the mean of laboratory means (standard uncertainty u_{char}): 123.13 mg/kg

The following statistical tests were carried out (at significance levels 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 skewness and kurtosis

The main features are as follows:

- *Scheffé*- und *Snedecor*-F-test: Data sets differ significantly.
- *Bartlett* test: Variances are homogeneous.
- *Cochran* test: One outlier (L02, significance level 0.05).
- *Dixon* and *Grubbs* tests: No outliers.
- *Nalimov* test: One outlier (L11, significance level 0.05).
- *Kolmogorov-Smirnov* and skewness/kurtosis test: Data are normally distributed.

No data were removed from further evaluation on the basis of the statistical tests. The mean of laboratory means w_{char} of 3554 mg/kg TPH was taken as the best estimate for the value to be certified, and the standard uncertainty of the mean of laboratory means $u_{char} = s/n^{½}$ (n = number of laboratories) of 123.13 mg/kg ($u_{char,r} = u_{char} / w_{char}$ = 0.034645) was taken as best estimate for the uncertainty contribution from the intercomparison.
Figure 5 depicts the individual results.

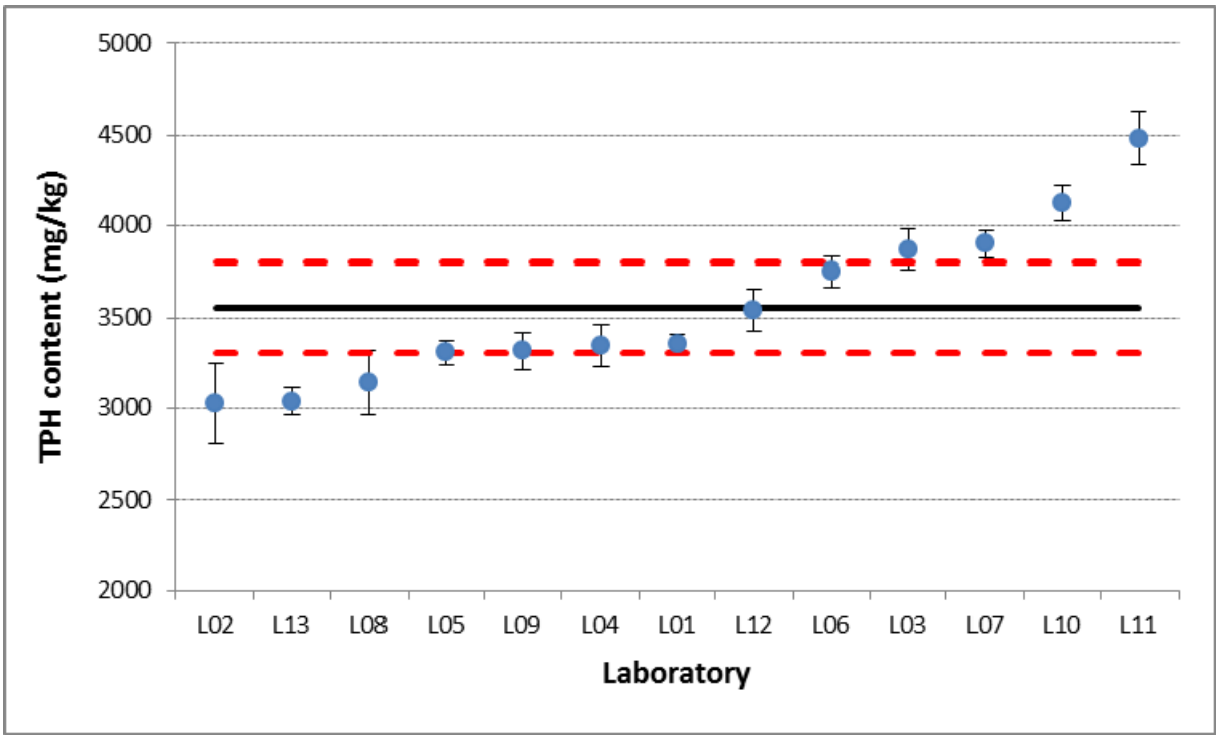


Fig. 5: Results of the characterisation exercise (see Table 6) with mean of means w_{char} (full line) and 95% confidence interval ($w_{char} \pm 2\ u_{char}$, dashed lines).

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 16703:2005 having been quantified in relation to the certified calibration standard BAM-K010. Thus, the stated references for BAM-U021 are ISO 16703:2005 and the calibration standard BAM-K010 mentioned for this purpose therein. Given the method used and the convention applied, the certified value is traceable to the SI.

5.2.3 Certified value and combined uncertainty

The estimate for the certified value w_{cert} in clause 5.2.1 (TPH mass fraction) must be corrected for the purity of the calibration standard used in all of the experiments according to

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

The corresponding combined uncertainty must appropriately be composed of the uncertainty of characterisation u_{char}, the contribution due the inhomogeneity between bottles u_{bb}, and the uncertainty due the purity correction u_{pur} according to

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

where the index *r* refers to the corresponding relative uncertainties. The purity and its corresponding uncertainty were taken from the certificate of BAM-K010 as f_{pur} = 0.967 and u_{pur} = 0.009, u_{char} is given in Clause 5.2.1, and u_{bb} in Clause 3.
The final values are given in Table 5 where the coverage factor for the expanded uncertainty is k = 2. The value and the expanded uncertainty are rounded according to the recommendations of [8] and are given with respect to raw sample mass. The water content was seen to remain stable if the material is handled according to the instructions in the certificate (see also Clause 6).

Table 5: Certified TPH content of BAM-U021 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)	3554	128	256
After rounding	**3560**	**130**	**260**

6 Information on the proper use of BAM-U021

6.1 Shelf life

From the initial stability study no shelf life restrictions at storage temperatures of 4 °C or below can be estimated. Since higher temperatures during the dispatch to the end user may occur the validity of the certified properties is set to 24 months beginning with the dispatch of the material from BAM. The validity of this information will be maintained by the post-certification monitoring.

6.2 Transport, storage and use

The stability of the TPH content allows dispatch of the material at ambient temperature. On receiving, it is to be stored at -20 °C. Before withdrawing a sub-sample the bottle has to have reached ambient temperature. Thereafter, the bottle must be closed tightly and stored at -20 °C. The water content remains stable when the material is treated as described. It is strongly recommended to apply a calibration standard BAM-K010 as mentioned in ISO 16703:2005.

6.3 Safety instructions

The sediment was not sterilised, however, it is supposed to not exhibit any biological activity due to having been dried to constant mass. 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 oils.

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 BAM Federal Institute for Materials Research and Testing 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

[1] ISO 16703:2005. Soil Quality - Determination of content of hydrocarbon in the range of C_{10} to C_{40} by gas chromatography

[2] ISO 9377-2:2000. Water quality - Determination of hydrocarbon index – Part 2: Method using solvent extraction and gas chromatography

[3] EN 14039:2004. Characterization of waste - Determination of hydrocarbon content in the range of C_{10} to C_{40} by gas chromatography

[4] R. Becker, M. Koch, S. Wachholz, T. Win, Quantification of total petrol hydrocarbons (TPH) in soil by IR-spectrometry and gas chromatography – conclusions from three proficiency testing rounds, *Accred. Qual. Assur.* (2002) 7, 286 - 289

[5] R. Becker, H.-G. Buge, W. Bremser, I. Nehls, Mineral oil content in sediments and soils: comparability, traceability and a certified reference material for quality assurance, *Anal. Bioanal. Chem*. (2006) 385, 645 - 651

[6] ISO Guide 35:2006. Reference materials -- General and statistical principles for certification. ISO, Geneva

[7] A. Lamberty, H. Schimmel, J. Pauwels. The study of the stability of reference materials by isochronous measurements. *Fres. J. Anal. Chem.* (1998) 360:359:361

[8] ISO/IEC Guide 98-3:2008: Uncertainty of measurement – Part 3: Guide to the expression of uncertainty in measurement. ISO, Geneva 2008, ISBN 92-67-10188-9

[9] SoftCRM V.1.22 (developed and funded under Contract SMT4 - CT98 - 6533 of the STANDARDS, MEASUREMENTS & TESTING PROGRAMME)

ANNEX A: Homogeneity and stability, measurement data

Results of the homogeneity study on BAM-U021. SD – Standard deviation.

Bottle	**Replicate**				
No.	**1** (mg/kg)	**2** (mg/kg)	**3** (mg/kg)	Mean (mg/kg)	**SD** (mg/kg)
24	2853	3066	2969	2963	107
44	2974	3069	2970	3004	56
64	3020	2893	3221	3045	166
80	3029	3021	2994	3015	19
102	3123	3029	3017	3056	58
125	3116	3118	2997	3077	69
145	3067	3002	3167	3079	83
165	3230	3126	3154	3170	54
185	3028	3018	2895	2980	74
201	3162	3153	3001	3105	91
224	2877	3137	3026	3013	130
244	3003	3018	2983	3001	18
265	3059	3052	2910	3007	84
281	3041	3001	2985	3009	29
303	3303	3001	3136	3147	151

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	153123.163	14	10937.3688	1.343	0.24076	2.037
within bottles	244211.033	30	8140.36778			
total	397334.196	44				

The grand mean of the homogeneity study is 3041 mg/kg. According to ISO Guide 35 the uncertainty between bottles $u_{bb} = s_{bb}$ is the result of eq. (1) which is greatest than that of eq. (2) and amounts to 30.53 mg/kg.

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

$$S_{bb} = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{N(n-1)}} \quad (2)$$

where:

n = Number of replicate determinations per sample
N = Number of bottles analysed

The relative value $u_{bb,r}$ is $u_{bb}/3041 = 0.016263$.

Results of the stability study on BAM-U021.

T = 4 °C

1 Month	TPH (mg/kg)	3 Months	TPH (mg/kg)	6 Months	TPH (mg/kg)
53-1	3127	**54-1**	3260	**55-1**	3047
53-2	3058	**54-2**	3091	**55-2**	2949
53-3	2919	**54-3**	3124	**55-3**	2980
Mean	3035		3158		2992
SD	105.94		89.58		50.09

T = 20 °C

1 Month	TPH (mg/kg)	3 Months	TPH (mg/kg)	6 Months	TPH (mg/kg)
62-1	2955	**63-1**	2922	**65-1**	2980
62-2	3021	**63-2**	3367	**65-2**	2900
62-3	3045	**63-3**	3034	**65-3**	2955
Mean	3007		3108		2945
SD	46.60		231.47		40.93

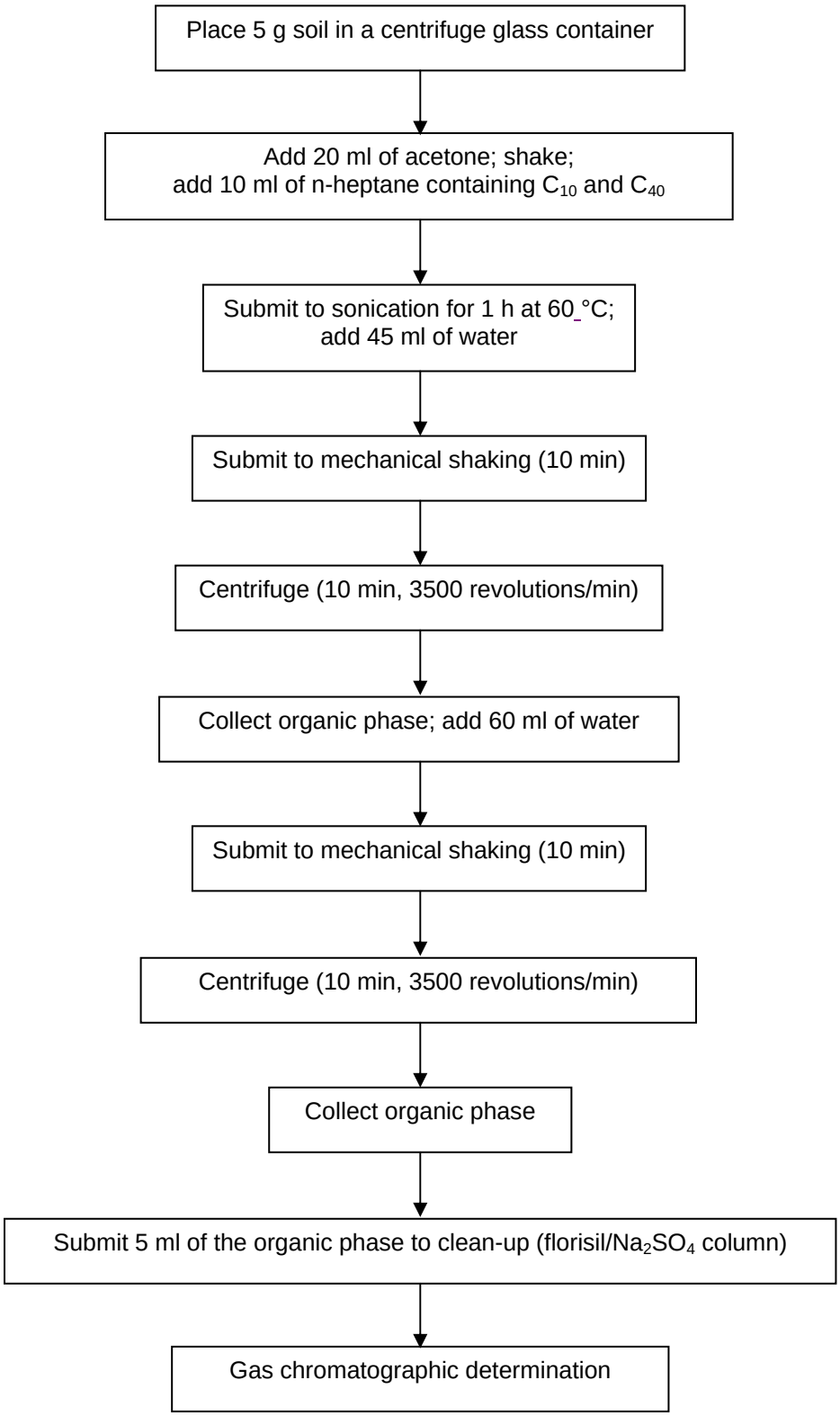
T= 40 °C

1 Month	TPH (mg/kg)	3 Months	TPH (mg/kg)	6 Months	TPH (mg/kg)
73-1	2960	**74-1**	2952	**75-1**	3034
73-2	2946	**74-2**	2995	**75-2**	3077
73-3	2914	**74-3**	2942	**75-3**	3052
Mean	2940		2963		3054
SD	23.58		28.16		21.59

T = 60 °C

1 Month	TPH (mg/kg)	3 Months	TPH (mg/kg)	6 Months	TPH (mg/kg)
77-1	3111	**78-1**	3070	**79-1**	2857
77-2	2976	**78-2**	2904	**79-2**	2869
77-3	2964	**78-3**	2903	**79-3**	2979
Mean	3017		2959		2902
SD	81.63		96.13		67.24

T = -20 °C

Since bottling	TPH (mg/kg)
45-1	2843
45-2	2965
45-3	2913
Mean	2907
SD	61.22

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