BAM-U015b: Mineral Oil Contaminated Sediment

Certification Report

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1 Introduction

Mineral oils are among the most important organic pollutants in environmental matrices and have been in the centre of concern of international standardisation bodies. Standardised procedures for the determination of total petrol hydrocarbons (TPH) in soil, water and waste have been developed [1-3]. Consequently, matrix reference materials are applied for quality assurance in routine laboratories in the course of proficiency testing [4] and as certified reference materials [5].

As a matter of fact environmental contamination with mineral oil hydrocarbons originates from fossil fuels or related products such as lubricants. Therefore, only complex mixtures of hydrocarbons are observed and the measurand of interest is the sum of a boiling range to be defined. This definition of the boiling range, the extraction solvent, the clean-up inevitable to remove interfering components from the extracts and GC-FID as the compulsory determination method and the calibration with an adequate TPH mixture is laid down in [1-3]. Thus, TPH is a parameter necessarily to be defined by the method which has strictly to be followed.

The reference material BAM-U015b is meant to be used for the verification of the quantification of TPH according to ISO 16703:2005 (accuracy and precision) in sediments and closely related matrices such as soils. The candidate material was prepared at BAM from a “real-world” fresh water sediment 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 proficiency documented as participants in the proficiency testing scheme “Contaminated Sites” organised by BAM. BAM-U015b replaces ERM-CC015a which displayed a similar TPH content in fresh water sediment from another source and has meanwhile been sold out.

2 Production of the candidate material

2.1 Selection of the starting material

The fresh water sediment was sampled from the riverbed of River Elbe, near to the port of a former industrial site situated south of the city of Magdeburg, Saxony-Anhalt (Germany). The contamination with various pollutants including mineral oils originates from chemical and pharmaceutical industry in the region.

2.2 Preparation of the candidate material

The wet starting material (approx. 230 kg) was freeze-dried at first. A total of 103.5 kg of dry sediment matrix was obtained thereafter. Then, large particles of mineral and biological matter were removed from the dried bulk material by means of a sieve with 10 mm aperture. The remaining material (89.4 kg total) was passed through a pin mill to gently smash the brittle agglomerates yielding a total of 74.6 kg of material < 2.0 mm. After classification by means of an automatic sieving station a total amount of 53.6 kg of the fraction < 125 µm was gained.

Thereafter, this material was homogenised by means of a 120 L stainless steel barrel equipped with a mixing insert inside of the barrel for accelerating and improving the mixing intensity which was continuously moved in a drum hoop mixer (J. Engelsmann AG, Ludwigshafen; Germany) for approx. 31 h. Further homogenisation and bottling was achieved using a VIS type mixer (AMK, Aachen, Germany) with a helically shaped mixing blade which is inclined 45°. The trough is equipped with an automatic partitioning device that allows bottling of the individual units under precise gravimetric control.

A total of 730 units were bottled in 125 mL amber glass bottles containing (72.9 ± 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 the isomerism of the hydrocarbon components. Thus, TPH is a typical example for a measurand defined by the method as laid down in ISO 16703:2005. This definition includes the clean-up of extracts in order to remove inferring 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] has been used. For the measurements on the candidate material a BPX-5 capillary column (15 m x 0.23 mm x 1 µm) and the following instrumental conditions were employed.

Oven programme
50 °C (10 min) → 360 °C (10 min)
Heating rate: 30 °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

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

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-U015b

Measurand	**Value***	**Method**
Particle size range (µm)	0 – 125	Sieving
Water content (%)	2.54 ± 0.05	*Karl-Fischer*-Titration
Loss on drying (%)	2.49 ± 0.14	Gravimetry after drying to constant mass at 105 °C (DIN ISO 11465)
CHN-Analysis (%)	C: 8.91 ± 0.17 H: 1.17 ± 0.03 N: 0.41 ± 0.01	Combustion

* means and standard deviations (n = 3)

Figure 1 depicts the chromatogram of a typical extract of the material obtained with the analytical procedure mentioned in 2.3 and outlined in ANNEX D. The mineral oil pattern in this sediment is typical for this type of matrix with an aged contamination as it has been observed similarly before in comparable fresh water sediments including ERM-CC015 [5]. Characteristic features are the high boiling range exceeding C_{40} and the scarcely present n-alkanes as being typical for diesel (gas oil) contaminations. Figure 2 displays for comparison a chromatogram for the calibrant BAM-K010 which is composed of diesel oil and lubricating base oil (1:1).

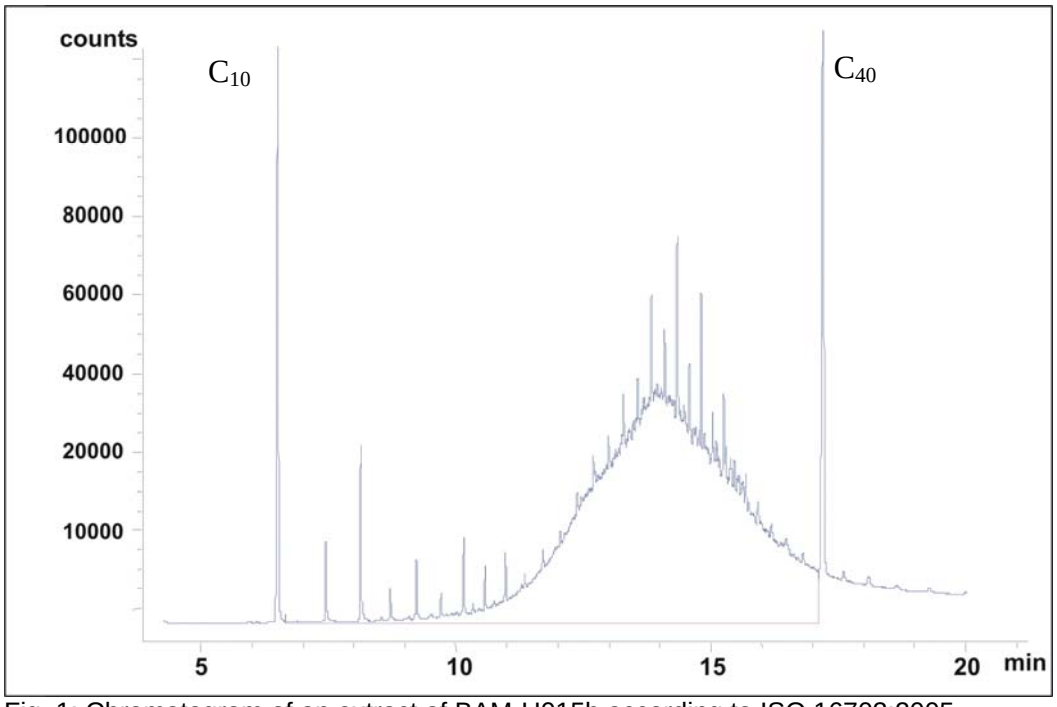


Fig. 1: Chromatogram of an extract of BAM-U015b according to ISO 16703:2005

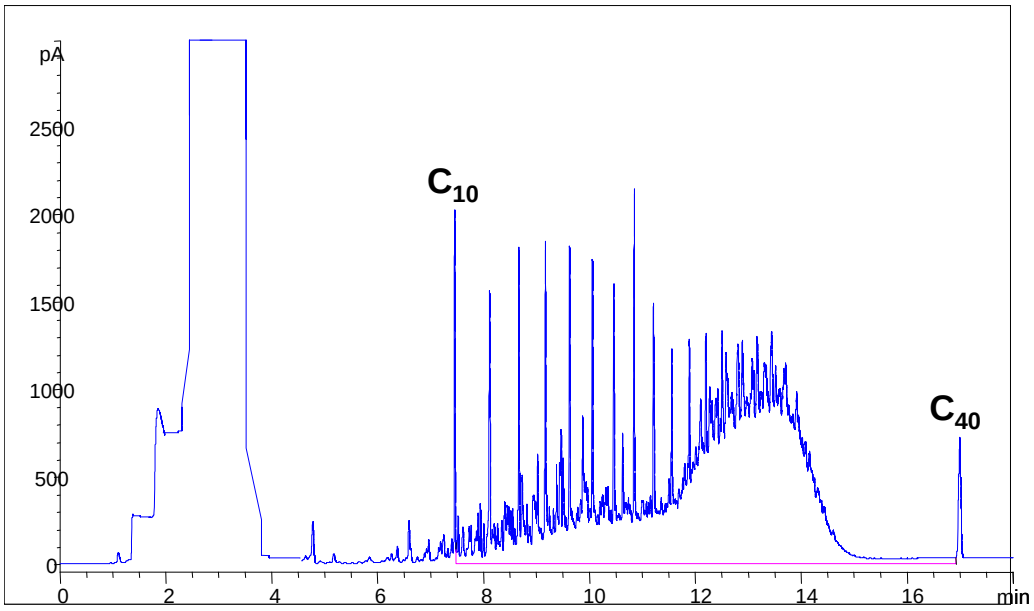


Fig. 2: Chromatogram of the calibration standard BAM-K010

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. Measurements revealed that this is the case with 5 g sample intake for a single determination. Therefore, this is the intake recommended on the certificate.

3 Homogeneity study

Twenty units were selected equidistantly from the whole set of 730 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 D. Three extractions from each of the 20 units were produced under repeatability conditions on three consecutive days.
Processed extracts were analysed by GC-FID using the method given in clause 2.3 under repeatability conditions in the course of which all 60 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 C. No evidence suggesting a rejection of the hypothesis that the material is sufficiently homogeneous was observed and the uncertainty of the TPH content between the bottles u_{bb} was estimated as 14.166 mg/kg, yielding a relative uncertainty due to inhomogeneity $u_{bb,r}$ of 0.01626.

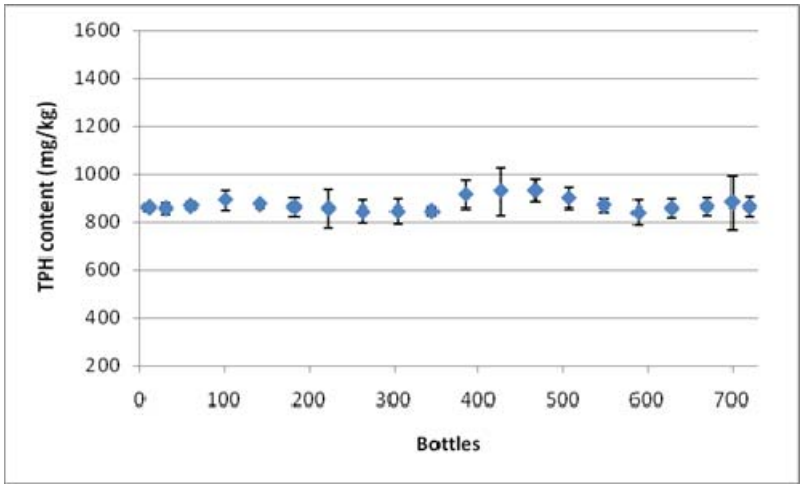


Fig. 3: Results of the homogeneity study

4 Stability study

4.1 Initial stability study

From experience [5] a temperature-driven deterioration of the TPH content was to be expected also for this material. Fifteen 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 12 months as shown in Table 3. After the respective periods of time individual units were stored at -20 °C. All units were analysed for TPH in triplicate using the method described above under repeatability conditions together with two reference samples which had been kept at -20 °C since bottling. For the individual data see ANNEX C.

Table 3: Accelerated ageing of exposed samples[1)]

Ageing [Months]	+4 °C	+20 °C	+40 °C	+60 °C	Remark
1	356	365	375	379	initial study
3	357	366	376	380	initial study
6	358	367	377	381	initial study
12	359	368	378	-	initial study
24	360	369	-	-	2)
36	361	370	-	-	2)
48	362	371	-	-	2)
60	363	372	-	-	2)

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

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.

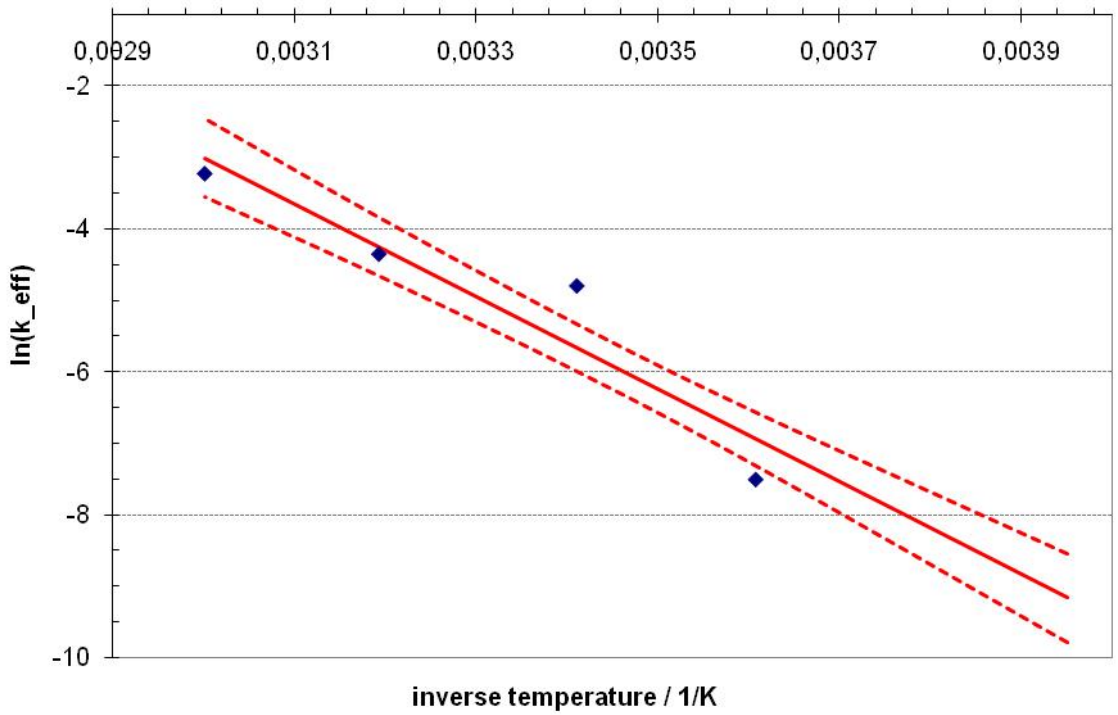


Fig. 4: Dependence of the degradation rate ln(k_eff) of TPH in BAM-U015b on the inverse temperature(semilogarithmic plot)

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. The estimated activation energy ΔE is 53.96 kJ/mol. 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 5.

Table 5: Estimation of shelf life

T [°C]	Months	Years
-20	568.1	47.3
4	78.8	6.6
20	22.9	1.9
40	5.2	0.4
60	1.3	0.1

Although shelf life at a storage temperature of -20 °C is quite considerable, any exposure to room or even higher temperatures may drastically reduce the time of validity of BAM-U015b. 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 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 Selection of participating laboratories

A total of 12 laboratories were invited to participate in the certification exercise. They were selected on grounds of a satisfactory performance in two recent proficiency testing rounds on TPH analysis in soil operated by BAM. 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, two different BAM laboratories took part in this exercise. The participants are listed in alphabetical order (not identical with the numbering in the data table below).

Analysen Service GmbH - Umwelt- und Öllabor	04277	Leipzig
Analytik Institut Rietzler GmbH	90471	Nürnberg
ARGUS Umweltbiotechnologie GmbH	12277	Berlin
BAM Bundesanstalt für Materialforschung und -prüfung, AG 1.21	12489	Berlin
BAM Bundesanstalt für Materialforschung und -prüfung, AG 1.23	12489	Berlin
chemlab - Gesellschaft für Analytik und Umweltberatung mbH	64625	Bensheim
Freie und Hansestadt Hamburg - Institut für Hygiene und Umwelt	20539	Hamburg
GDF SUEZ E&P DEUTSCHLAND GMBH	29416	Steinitz
ICA - Institut für Chemische Analytik GmbH	04229	Leipzig
IfE - Analytik GmbH	04347	Leipzig
Institut Koldingen GmbH	31157	Sarstedt
WESSLING Laboratorien GmbH	30625	Hannover
WESSLING Laboratorien GmbH	82061	Neuried
WESSLING Laboratorien GmbH	69190	Walldorf

5.2 Design of the study

Two units of the candidate material were to be analysed by each laboratory in triplicate. The information that the level of content was to be expected between 500 mg/kg and 1500 mg/kg was provided as well as certified calibration standard BAM-K010 to ensure equal conditions as far as technically feasible (see also clause 5.3.3). Two TPH solutions in n-heptane unknown to the participants were also distributed and the participants were asked to quantify the TPH content. Results returned to BAM were scrutinised for consistency and a few obvious transcription errors were corrected after clarification with the respective laboratories.

5.3 Evaluation of results and certified values

The results of the certification study were evaluated in accordance with ISO Guide 35 [8]. The computer software SoftCRM [9] was partially used for statistical tests and data treatment.

5.3.1 Technical evaluation

All participants in the certification study were asked to determine the TPH content of the two TPH control solutions along with measurements on BAM-U015b. The results are summarised in Figure 5.

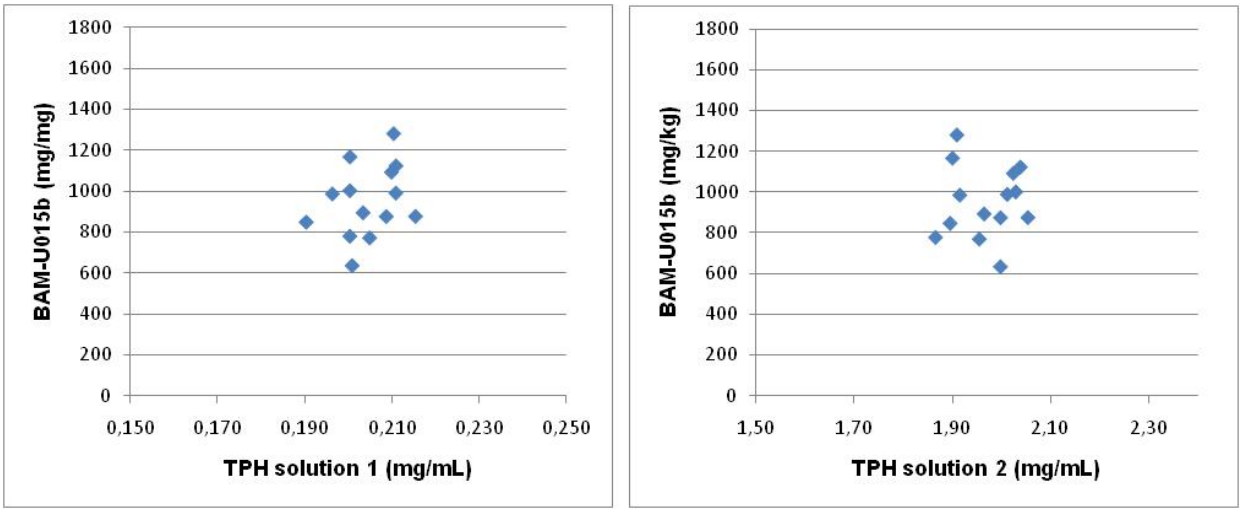


Fig. 5: Plot of the mean values found by the laboratories for the candidate material against the recovery of the TPH control solutions 1 and 2.

For each control solution, the mean values of the laboratories were plotted against the recovery the laboratories attained for the material BAM-U015b. There are no significant outlying observations and no data were discarded on grounds of inconsistency with the whole data set.

5.3.2 Statistical evaluation

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:

- the mean of laboratory means
- the standard deviation of the distribution of laboratory means, and the standard deviation of the mean of laboratory means
- the confidence interval of the mean of laboratory means at the 0.05 significance level

and 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 test for the verification of possible outlier indications
- Kolmogorov-Smirnov Test (Lilliefors version) for the normality test
- Test for skewness and kurtosis

The main features are as follows:

- *Scheffé*- und *Snedecor*-F-Test: Data sets differ significantly.
- *Bartlett*-Test: Variances are inhomogeneous (at the significance level of 0.01).
- *Cochran*-Test: Two outliers detected (no. L11 and L14, significance level 0.01).
- *Dixon*-, *Grubbs*- und *Nalimov*-Test: Laboratory means do not contain an outlier, however one Nalimov straggler, no. L12, significance level 0.05).
- *Kolmogorov-Smirnov* and skewness/kurtosis test: Based on the available data, the hypothesis of normality cannot be rejected.

Table 6: Data sets received from the participants in the certification study of BAM-U015b

Laboratory	**Sample A**			**Sample B**					
	# 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	912	920	900	870	884	882	895	7.9	0.9
L02	1000	970	920	1100	996	935	987	26.1	2.6
L03	884	821	938	832	792	823	848	21.7	2.6
L04	790	810	802	770	769	734	779	11.3	1.4
L05	1037	1026	983	979	963	1029	1003	12.8	1.3
L06	771	776	775	764	762	777	771	2.6	0.3
L07	1123	1116	1082	1119	1082	1041	1094	13.0	1.2
L08	933	1059	997	969	1024	963	991	18.6	1.9
L09	884	882	854	922	861	858	877	10.4	1.2
L10	606	638	628	636	662	640	635	7.4	1.2
L11	1206	1079	1086	1414	1228	998	1169	60.3	5.2
L12	1137	1232	1245	1356	1358	1367	1283	38.0	3.0
L13	833	830	880	868	953	891	876	18.4	2.1
L14	1143	1022	1267	1119	1041	1156	1125	36.1	3.2

[a] standard deviation
[b] relative standard deviation

No data were removed from further evaluation on the basis of the statistical tests. The mean of laboratory means of 952.188 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 of 46.877 mg/kg TPH as the uncertainty contribution from characterisation u_{char} by intercomparison. Figure 6 depicts the individual results.

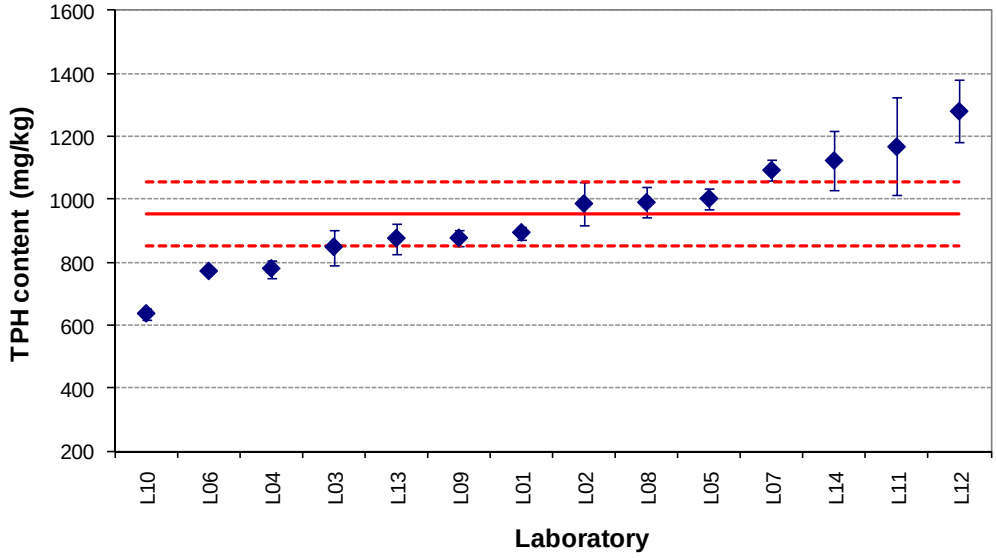


Fig. 6: Results of the characterisation exercise (see Table 6) with mean of means and confidence intervals.

5.3.3 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-U015b 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.

5.3.4 Certified value and combined uncertainty

The estimate of clause 5.3.2 for the certified value w_{cert} (TPH mass fraction) must be corrected for the purity of the calibration standard used in all of the experiments according to

$$w_{cert} = w_{char} * f_{pur}$$

The corresponding combined uncertainty must appropriately be composed of the uncertainty of characterisation u_{char}, the contribution from a possibly undetected inhomogeneity u_{bb}, and the uncertainty of the purity correction u_{pur} according to

$$u_{com,r}^2 = u_{char,r}^2 + u_{bb,r}^2 + u_{pur,r}^2$$

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 5.3.2, and u_{bb} in Clause 3.
The final values are given in Table 7 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 7: Certified TPH content of BAM-U015b in mg/kg

Certified value, corrected for purity	Combined uncertainty of the certified value	Expanded uncertainty of the certified value
920	**49**	**100**

6 Information on the proper use of BAM-U015b

6.1 Shelf life

From the initial stability study a preliminary shelf life of 3 years at storage temperatures not higher than 4 °C is estimated. Since the dispatch to the end user may occur at any time during this period the certified properties will be valid for 12 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: Result reporting sheet

Zertifizierungsringversuch:

Mineralölkohlenwasserstoffe (MKW) in Sediment

Besonderheiten: - Führen Sie je Probe 3 Einzelbestimmungen aus
- Bitte beachten Sie die Dimensionen und die Probennummern

Einwaagen: ***(bitte jeweils ca. 5 Gramm einwiegen!)***

Sediment		1	2	3
Probe A	**g**			
	Datum			
Probe B	**g**			
	Datum			

MKW-Gehaltsbestimmungen:

Sediment		1	2	3
Probe A	**mg/kg**			
	Datum			
Probe B	**mg/kg**			
	Datum			

Verzichten Sie hier auf die Angabe von Nachkommastellen !

Kontrollmessungen:

		1	2
Verfahrens-blindwert	**mg/kg**		
	Datum		

Unbekannte Lösungen 1 und 2:
(enthalten bereits die Integrationsbereichsmarker n-Decan und Tetracontan)
(sind direkt zu injizieren, eine Verdünnung ist nicht erforderlich)

Lösung		1	2
Lösung 1	**mg/ml***		
	Counts		
	Datum		
Lösung 2	**mg/ml***		
	Counts		
	Datum		

Geben Sie hier bitte drei signifikante Stellen an !

Datum: 2004 Unterschrift: _____

ANNEX B: Methods reporting sheet

Prüflaboratorium:

Bitte machen Sie kurze Angaben zu Ihren Geräte- und Messbedingungen !
(Zutreffendes ankreuzen bzw. geforderte Eintragungen vornehmen !)

Mineralölkohlenwasserstoffe (MKW) in Sediment

Probenvorbereitung

Extraktionsverfahren: ☐

Extraktionsdauer [h]: ☐

Extraktionstemperatur [°C]: ☐ (Angabe bei Soxhlet nicht erforderlich)

Lösungsmittel: ☐ ☐

Wenn Soxhletextraktion angewendet:
Volumen der Extraktionskammer [ml]: ☐
Anzahl der Extraktionszyklen (geschätzt): ☐

Wurde nach dem Entwurf ISO 16703:2005
☐ ja ☐ nein

Clean-up gemäß ISO 16703:2005 durchgeführt? ☐ ja ☐ nein

☐

GC-Messbedingungen

Gerätetyp: _____

Detektor: ☐ FID

Säule (Abmessungen, Phase, etc): _____

Trägergas/Fluss: _____

Probenaufgabeverfahren: _____

Aufgabevolumen [µl]: _____

Temperaturprogramm: _____

Auswertung: ☐ Retentionszeitbereich C10 bis C40

Art des verwendeten externen Standards: ☐ BAM-K010 oder BAM CRM 5004

Hersteller des Standards: ☐ andere: _____

Bitte Verdünnungsschritte beschreiben:

5-Punkt-Kalibrierung erfolgt ? ☐ ja ☐ wenn nein, Anzahl der Kalibrierpunkte (> 5)

(Mindestanforderung: 5 Kalibrierpunkte)

MKW-Kalibrierkonzentrationen [mg/ml]:

Niedrigste Kalibrierkonzentration:		Counts	
Höchste Kalibrierkonzentration:		Counts	

Wurden die Lösungen 1 und/oder 2 verdünnt? ☐ nein ☐ ja

Anmerkung: ***Eine Verdünnung der messfertigen Lösungen ist im Normalfall nicht erforderlich!***

Wiederfindungsrate gemäß ISO 16703:2005, Pkt. 9.4.2 (in %):

ANNEX C: Homogeneity and stability, measurement data

Results of the homogeneity study on BAM-U015b, s – Standard deviation.

Bottle	Replicate				
No.	**1** (mg/kg)	**2** (mg/kg)	**3** (mg/kg)	Mean (mg/kg)	**s** (mg/kg)
10	874	850	855	860	12.9
30	877	852	835	855	21.1
60	870	851	876	866	13.2
101	934	870	866	890	38.2
141	890	864	864	873	14.7
182	818	893	872	861	39.1
223	899	904	762	855	80.8
263	869	870	788	842	47.0
304	887	857	787	844	51.1
345	851	824	853	843	16.2
385	944	952	843	913	60.9
426	816	1004	964	928	98.8
467	974	934	880	929	47.3
507	851	940	901	897	44.9
548	898	862	844	868	27.4
589	895	800	819	838	50.6
629	860	890	815	855	37.6
670	854	902	832	863	35.3
700	749	941	950	880	113.4
720	854	907	826	862	41.2

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	42563.13	19	2240.16	0.832	0.659	1.853
within bottles	107698.24	40	2692.46			
total	150261.37	59				

The grand mean of the homogeneity study is 871.026 mg/kg. The uncertainty between bottles u_{bb} is calculated according to (1) and amounts to 14.166 mg/kg

$$u_{bb} = \frac{s_{method}}{\sqrt{n}} \sqrt[4]{\frac{2}{N(n-1)}} \quad (1)$$

where:

s_{method} = Method variability ($=\sqrt{MS_{within}}$)

n = Number of replicate determinations per sample

N = Number of bottles analysed

The relative value $u_{bb,r}$ is u_{bb}/871.026 = 0.016263

Results of the stability study on BAM-U015b. Temperatures, ageing periods and bottle numbers.

T = 4 °C

1 Month	TPH (mg/kg)	3 Months	TPH (mg/kg)	6 Months	TPH (mg/kg)	12 Months	TPH (mg/kg)
356-1	**985**	**357-1**	**967**	**358-1**	**947**	**359-1**	**1035**
356-2	**1143**	**357-2**	**1006**	**358-2**	**1020**	**359-2**	**973**
356-3	**1021**	**357-3**	**958**	**358-3**	**1055**	**359-3**	**1039**
Mean	1049.67		977.00		1007.33		1015.67
s	67.61		20.83		44.99		30.21

T = 20 °C

1 Month	TPH (mg/kg)	3 Months	TPH (mg/kg)	6 Months	TPH (mg/kg)	12 Months	TPH (mg/kg)
365-1	**1001**	**366-1**	**917**	**367-1**	**941**	**378-1**	**893**
365-2	**1007**	**366-2**	**1069**	**367-2**	**1023**	**378-2**	**853**
365-3	**1042**	**366-3**	**963**	**367-3**	**945**	**378-3**	**951**
Mean	1016.67		983.00		969.67		899.00
s	18.08		63.64		37.75		40.23

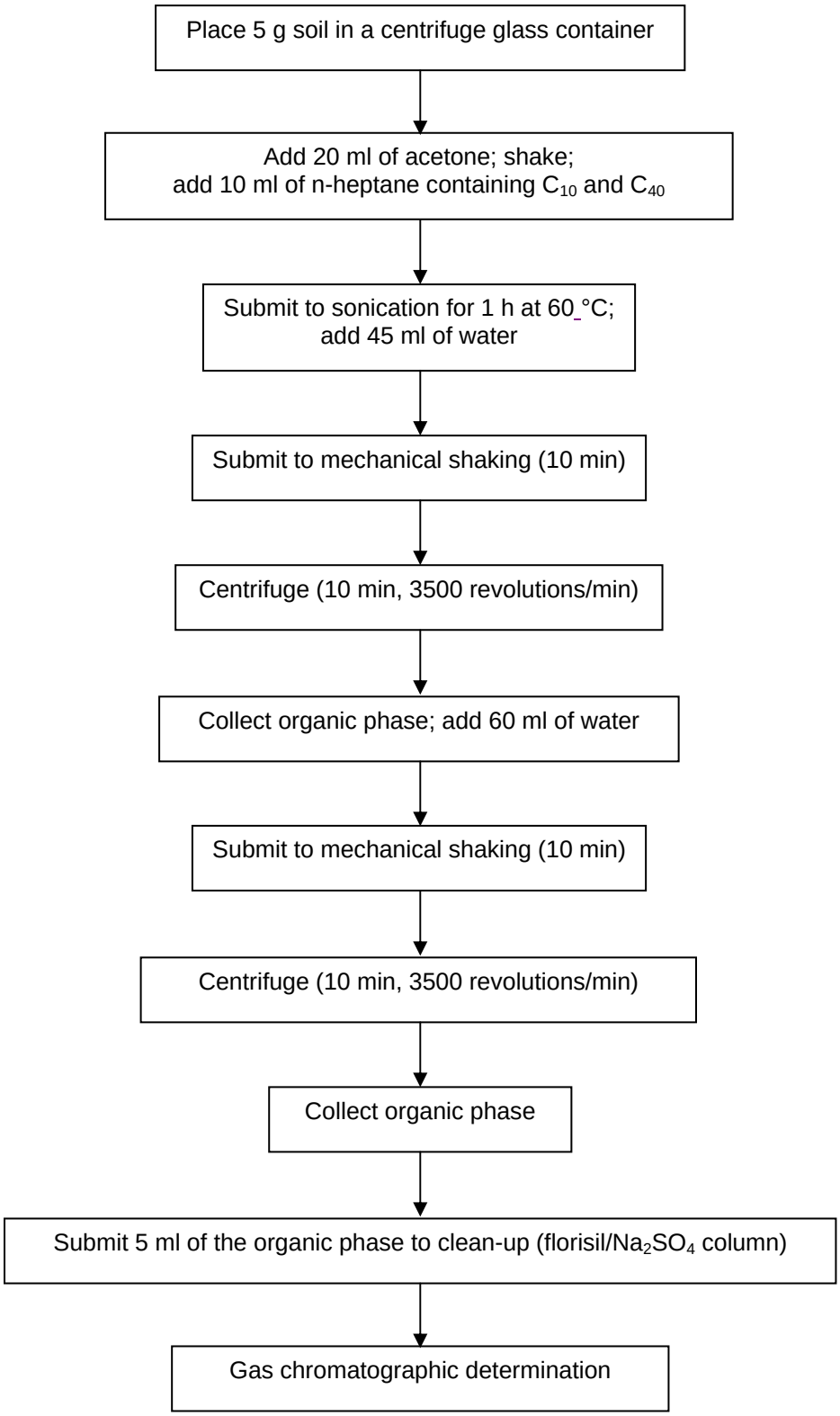
T= 40 °C

1 Month	TPH (mg/kg)	3 Months	TPH (mg/kg)	6 Months	TPH (mg/kg)	12 Months	TPH (mg/kg)
375-1	**857**	**376-1**	**902**	**377-1**	**898**	**378-1**	**784**
375-2	**889**	**376-2**	**957**	**377-2**	**887**	**378-2**	**783**
375-3	**967**	**376-3**	**987**	**377-3**	**821**	**378-3**	**884**
Mean	904.33		948.67		868.67		817.00
s	46.20		35.20		34.00		47.38

T = 60 °C

1 Month	TPH (mg/kg)	3 Months	TPH (mg/kg)	6 Months	TPH (mg/kg)
379-1	**820**	**380-1**	799	**381-1**	785
379-2	**908**	**380-2**	795	**381-2**	717
379-3	**936**	**380-3**	826	**381-3**	807
Mean	888.00		806.67		769.67
s	49.42		13.77		38.31

T = -20 °C

12 Months	TPH (mg/kg)	12 Months	TPH (mg/kg)
348-1	914	**349-1**	988
348-2	971	**349-2**	1059
348-3	1059	**349-3**	1001
Mean	981.33		1016.00
s	59.65		30.87

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