ERM-CC015a: Mineral oil contaminated sediment

Certification Report

ausverkauft / out of stock

R. Becker, H.-G. Buge, W. Bremser

Federal Institute for Materials Research and Testing (BAM)
Division I.2: “Organic Analytical Chemistry; Reference Materials”
Richard-Willstätter-Strasse 11

D-12489 Berlin, Germany

Sales

e-mail: sales.crm@bam.de
internet: www.webshop.bam.de

Contents

1 Introduction 4
2 Production of the candidate material 5
2.1 Selection of the starting material 5
2.2 Preparation of the candidate material 5
2.3 Analytical method 6
2.4 Characterisation of the matrix and the TPH composition 6
2.5 Minimum sample intake 8
3 Homogeneity study 8
4 Stability study 9
4.1 Initial stability study 9
4.2 Post-certification stability monitoring 11
5 Certification study 11
5.1 Selection of participating laboratories 11
5.2 Design of the study 11
5.3 Evaluation of results and certified values 11
5.3.1 Technical evaluation 11
5.3.2 Statistical evaluation 12
5.3.3 Traceability 13
5.3.4 Certified value and combined uncertainty 13
6 Information on the proper use of ERM-CC015a 14
6.1 Shelf life 14
6.2 Transport, storage and use 14
6.3 Safety instructions 14
6.4 Legal notice 14
7 References 14
ANNEX A - D 15

1 Introduction

Mineral oils are among the most important organic pollutants in environmental matrices and have been in the centre of concern with 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 material. 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 the determination method (GC/FID) including the calibration with an adequate TPH mixture is laid down in [1]. Thus, TPH is a parameter necessarily to be defined by the method which has strictly to be followed. The reference material ERM-CC015a is meant to be used for the verification of the quantification of TPH according to ISO/FDIS 1607:2003 (accuracy and precision) in sediments and closely related matrices such as soils. The candidate material to be certified has been prepared at BAM from a “real-world” fresh water sediment and characterised with regard to homogeneity and stability of the TPH content. A total of 12 laboratories selected on basis of experience and documented proficiency were invited to participate in the certification study on this candidate material. Following internationally accepted procedures the certified mass fraction of TPH, its uncertainty, the shelf life and the minimum amount for a single determination were evaluated. ERM-CC015a replaces ERM-CC015 which displayed a similar TPH content in a 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 a sediment trap in River Weisse Elster, near the city of Leipzig, Saxony (Germany). The contamination with various pollutants including mineral oils originates from past mining as well as municipal sewage farms and the chemical industry. The sampling site and the treatment of its contamination are described in [5].

2.2 Preparation of the candidate material

The starting material contained little mineral components and minor amounts of plant parts were removed manually. The bulk material (104 kg) was air dried to constant weight and then passed through a pin mill to smash the brittle agglomerates the material was composed of. After classification by means of an automatic sieving station 29.05 kg of the fraction < 125 µm were collected. This material was homogenised by means of a 120 L stainless steel barrel placed in a drum hoop mixer for 6 h. Further homogenisation and bottling was done using a version of the so-called “cross-riffling” procedure [6], a service-proved scheme of partitioning and back mixing, depicted in Fig. 1.

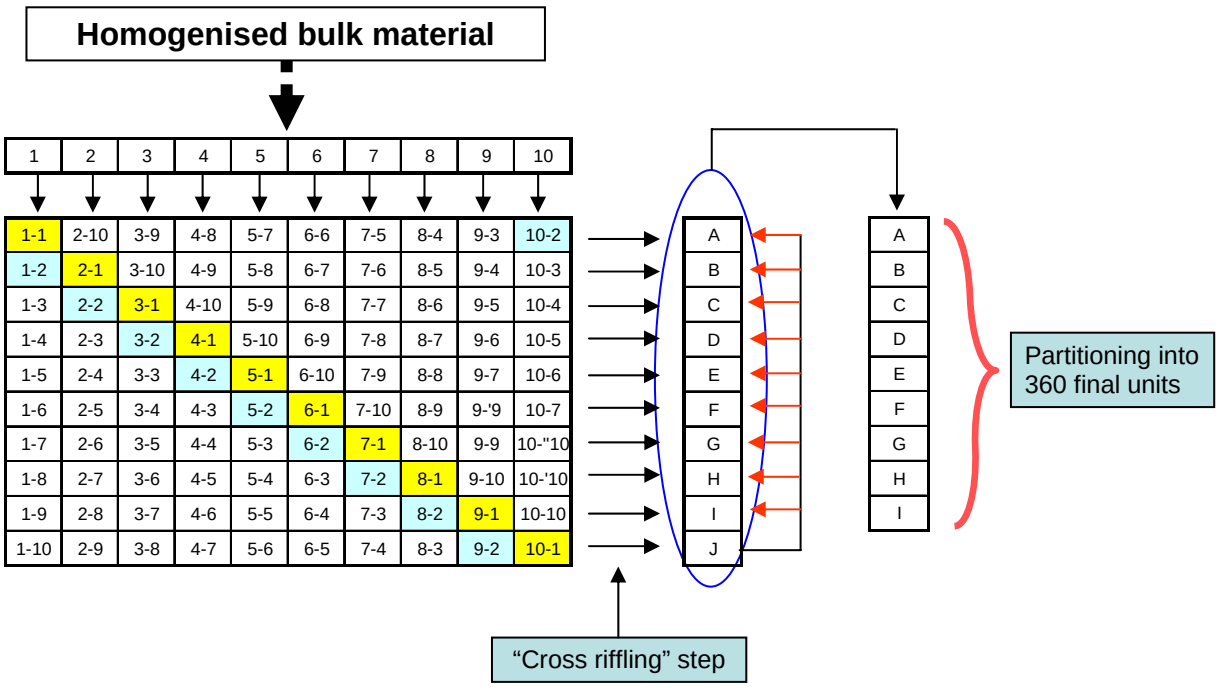


Fig. 1: Cross-riffling principle. The bulk material is divided into 10 sub-samples which are further partitioned and mixed again as depicted. Then, sub-sample J is distributed over sub-samples A – I. These 9 remaining sub-samples are subsequently partitioned by means of a spinning riffler with eight tubes (resulting in 9 x 8 sub-samples) and further divided into 360 sub-samples using a riffler with ten tubes and combining two sub-samples in a finally bottled unit.

A total of 360 units were bottled in 125 mL amber glass bottles containing (81,5 ± 0,4) g 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.

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 yield signals proportional to the actual amount of C and H over a wide range of content. Thus, TPH is a typical example for a measurand defined by the method as laid down in ISO/FDIS 16703:2003. 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 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-K10[1] was 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 program
50°C (10 min) → 360°C (10 min)
Heating rate: 30°C/min
Injection volume: 3µL
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

The sample preparation is outlined in ANNEX D.

2.4 Characterisation of the matrix and the TPH composition

Table 1: Matrix characterisation of ERM-CC015a

Measurand	**Value**	**Method**
Particle size range	0 – 125 µm	Sieving
Water content	(5,72 ± 0,10) %	*Karl-Fischer*-Titration
Drying loss	(5,60 ± 0,10) %	Gravimetry after drying to constant weight at 105°C (DIN ISO 11465)
Total organic carbon	(84 ± 8) mg/g	DIN ISO 10694
Total inorganic carbon	(0,60 ± 0,04) mg/g	DIN ISO 10694
CHN-Analysis (in %)	C: 8,45 ± 0,02; H: 1,81 ± 0,01; N: 0,623 ± 0,01	Combustion
pH	5,78 ± 0,01	E DIN ISO 10390

Table 1 comprises the chemical characterisation of the matrix of the candidate material. The relative high water content is at equilibrium with the atmosphere under typical laboratory conditions and corresponds to the relative high content of organic carbon.
Figure 2 depicts the chromatogram of a typical extract of the material obtained with the procedure outlined in ANNEX D and analysed as mentioned in clause 2.3 along with the a chromatogram of the employed calibration standard. The mineral oil pattern in this sediment seems to be 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. Characteristic features are the high boiling range exceeding C_{40}, the absence of distinct n-alkanes as being typical for diesel (gas oil) contaminations.

[1] Certified calibration standard BAM-K10 is mentioned for this purpose in ISO/FDIS 16703:2003 and available from BAM: www.webshop.bam.de

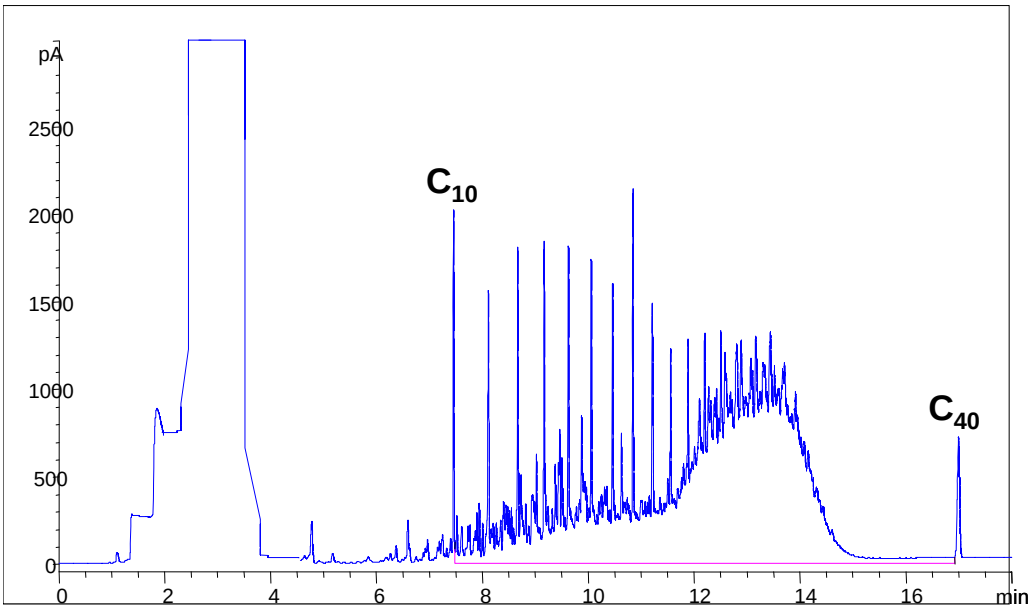


Fig. 2a: Chromatogram of the calibration standard BAM-K10

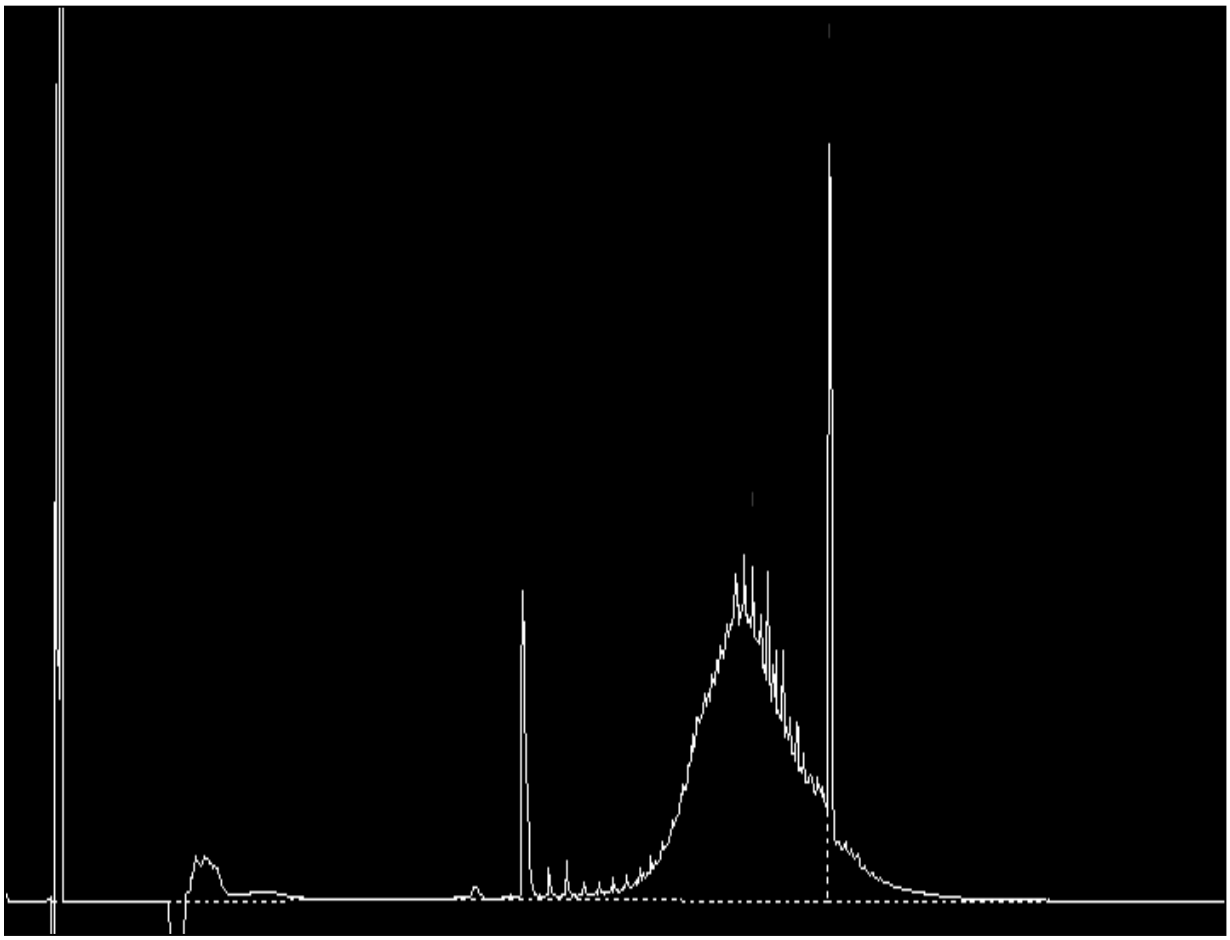


Fig. 2b: Chromatogram of an extract of ERM-CC015a according to ISO/FDIS 16703:2003

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 10 g sample intake for a single determination. Therefore, this is the intake recommended on the certificate.

3 Homogeneity study

15 units were selected equidistantly from the whole set of 360 bottles. They were analysed five times each according to ISO 16703:2003 using a sample intake of 5 g. The extraction procedure and instrumental parameters are given in clause 2.3. All 15 units were extracted once under repeatability conditions on five consecutive days.
Processed extracts were analysed by GC/FID using the method given in clause 2.3 under repeatability conditions in that all 75 extracts were quantified against one calibration after randomisation. No evidence suggesting a rejection of the hypothesis that the material is homogeneous was observed and the uncertainty of the TPH content between the bottles u_{bb} was estimated as 26,1 mg/kg for 5 g sample intake. For the measurement data and the analysis of variance see ANNEX C.

For simulating the influence of a larger sample intake on the estimation of possible inhomogeneity contributions, a bootstrap approach was used. Any two replicate runs were united into a single run, and all possible combinations of 2 x 2 runs out of five were covered. The limitation to 2 combined runs is due to the necessity of avoiding virtual data and correlations. Since the homogeneity data set contains a missing value (deleted outlier) for sample 150 in run 3, for this sample in all combinations containing run 3 a standard arrangement (1+2 and 4+5) was used. All 12 possible combinations were treated by ANOVA. The results for the total mean and the means of squared deviations (between and within) are given in the table below.

combination	mean	MS_between	MS_within	
1+2:3+4	1793.59	7728.84	6821.41	
1+2:3+5	1771.70	7742.81	7230.04	
1+2:4+5	1790.56	7686.20	6438.96	
1+3:4+5	1781.48	6417.53	5712.42	
1+3:2+4	1793.59	7728.84	3646.80	
1+3:2+5	1771.70	7742.81	4131.67	
1+4:2+3	1793.59	7728.84	6651.19	
1+4:2+5	1790.56	7686.20	7990.41	
1+4:3+5	1781.48	6417.53	9575.29	
1+5:2+3	1771.70	7742.81	3730.57	
1+5:2+4	1790.56	7686.20	3451.28	
1+5:3+4	1781.48	6417.53	5899.34	
averages	1784.33	7393.84	5939.95	
		u_bb from average MS		26.9620
		u_bb_r		**0.0151**

Since MS_between[2] is mainly determined by possible inhomogeneities, it does not largely vary over the different combinations, while MS_within is susceptible to sample intake and thus shows a more considerable variability. Averages for the mean and the means of squared deviations (between and within) were taken, and an u_{bb} was calculated accordingly. The value of 26,96 mg/kg is slightly larger than in the original study. It was used for the uncertainty calculations of clause 6 as a worst-case estimate.

[2] MS: Mean squares between and within samples, respectively

4 Stability study

4.1 Initial stability study

From experience 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 [7] accelerated ageing at temperatures between 4 and 60°C over periods of 3 weeks to 6 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 using the method described above under repeatability conditions together with 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

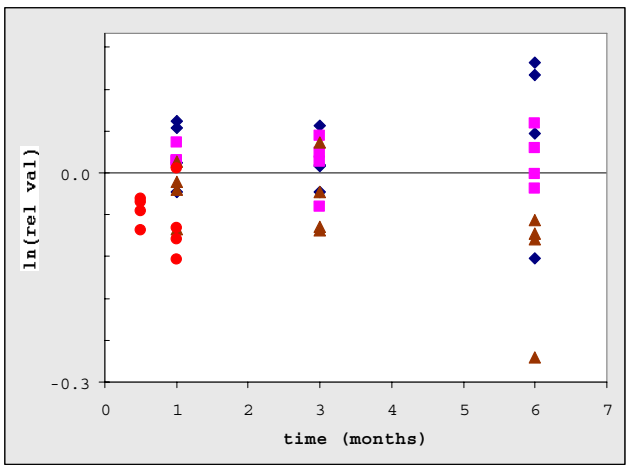
Ageing [Months]	+4°C	+20°C	+40°C	+60°C	Remark
0,5				42	initial study
1	37	65	44	43	initial study
3	38	66	45		initial study
6	39	67	46		initial study
12	40	68			1)
24	41	69			1)
36		70			1)
48		71			1)
60		72			1)

[1)] post certification monitoring

The dependence of the thermal degradation on time is expected to be exponential. As a first step in the data analysis, the logarithmic plots of the data as obtained were tested for trends separately for each degradation temperature.
A total of 12 extracts obtained from 3 reference samples evenly distributed over the whole measurement sequence were measured together with the exposed samples. Trend tests were applied to data in three different formats, i.e. to

i) all measured single values
ii) measured single value ratios
iii) means of the replicate measurements for all samples.

Note that if in case II the ratios are formed with respect to a common single reference value (normally the mean of single measurements taken for all reference samples) this constitutes a simple re-scaling of the data as used in case I and does not alter the results of the trend analysis.



Given the relatively large intermediate precision of the method and the relatively short sample exposure times, no trend could be observed for any of the degradation temperatures in case I (single values tested). Therefore, a data pre-treatment in accordance with case II was applied for which all data were sorted with respect to a) the day of preparation and b) the sequence of measurement of the samples. Ratios were formed with respect to the value measured for the closest reference sample in the sequence. This revealed a much clearer situation as can be seen from figure 3.

Fig. 3: Dependence on time of the ratio of the measured value for a sample and the closest reference in the sequence (degradation temperatures: 4°C - blue diamonds, 20°C - magenta squares, 40°C - brown triangles, and 60°C - red circles)

For 40°C and 60°C now a significant degradation is observed. When data are treated according to case III (trend test over the means of replicate measurements), a significant trend is observed for the highest degradation temperature. Note that in case I and III, the necessary values for the reference samples at zero time (start of the study) were taken from the homogeneity test.

Table 4 gives an overview of the slopes of the regression lines for the three data treatment cases, the significance of the regression, and the corresponding probability that the test statistic is exceeded by chance.

Table 4: Linear regression of the data obtained from the initial stability study

	temperature (°C)	-20	4	20	40	60
degradation rate from	single results	-0.000301	0.0053038	-0.001981	-0.006657	-0.036838
	single nested	-	0.0057249	-0.002344	-0.007076	-0.037383
	means	-0.000136	0.0059077	-0.000485	-0.021433	-0.03684
regression significant	single results	no	no	no	no	no
	single nested	-	no	no	yes	yes
	means	-	no	no	yes	-
P> value	single results	0.958	0.522	0.767	0.498	0.707
	single nested	-	0.607	0.920	0.042	0.039
	means	-	0.432	0.523	0.007	-

Note that case II data treatment by definition does not allow any statement on the reference samples, for case III treatment no statistics could be calculated for the reference and the highest degradation temperature since only two data points were available. The table will be updated during post-certification monitoring.

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 (case III format).

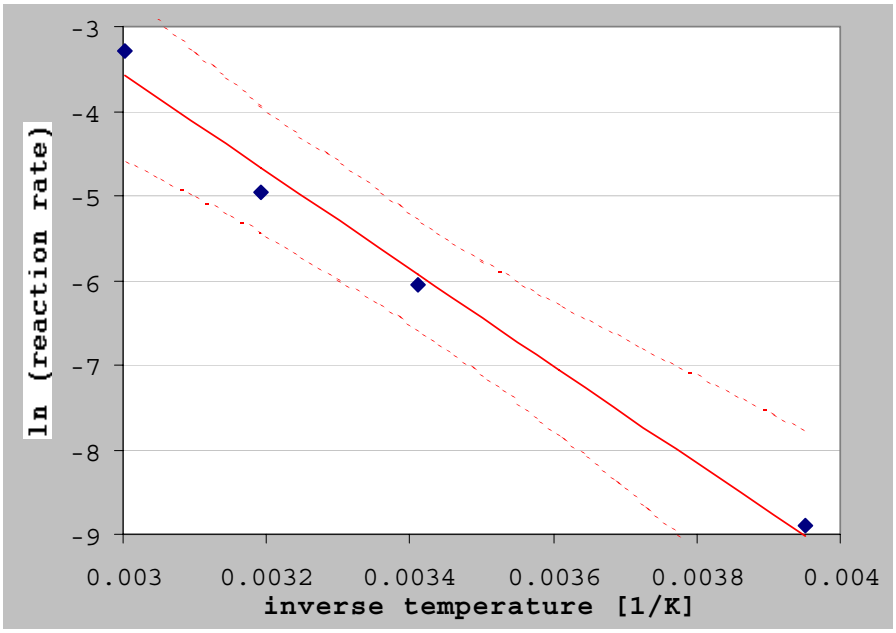


Fig. 4: Reaction rate for TPH in dependence on the inverse temperature (semi-logarithmic plot)

As can be seen from the plot, the temperature dependence can indeed be approximated by a straight line (as shown in the graph). The corresponding confidence interval for the line is also given in the figure. The estimated activation energy ΔE is 0,689 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 outside 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 results are given in table 5.

Table 5: Estimation of shelf life

time after which value falls out of U			months	years
at temperature	-20		169.0	14.1
at temperature	4		37.8	3.1
at temperature	20		13.7	1.1
at temperature	40		3.6	0.3
at temperature	60		1.0	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 ERM-CC015a. Therefore, a unique expiry date 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. Several units investigated during the initial stability study were stored again at +4°C or -20°C, respectively. That way, information on the long term stability of units of ERM-CC015a having been opened at least once for withdrawal of material is expected in the course of the post certification monitoring.

5 Certification study

5.1 Selection of participating laboratories

A total of 12 laboratories were invited to participate in the certification exercise. Nine of these laboratories 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/FDIS 16703:2003 and the declaration of commitment to comply with these requirements during the certification analyses. Additionally, three different BAM laboratories took part in this exercise.

5.2 Design of the study

Two units of the candidate material were to be analysed by each laboratory in triple. The information that the level of content was to be expected between 1000 and 4000 mg/kg was provided as well as certified calibration standard BAM-K10 to ensure equal conditions as far as technically feasible (see also clause 5.3.3). In addition, each participant received two control solutions with concentrations of mineral oil in n-heptane unknown to them. These solutions were prepared gravimetrically from the calibration standard BAM CRM 5004 such that they correspond to the lower and upper region of the calibration range. The standard procedure according to ISO/FDIS 16703:2003 had to be followed strictly and was to be documented (see ANNEX B).
Results for the mineral oil content were to be reported on basis of total mass intake, no dry mass determinations were asked for. 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 [9] and the specific requirements of the ERM agreement [10]. The computer software SoftCRM [11] 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 control solutions before the actual sample measurements were done. The results are listed in ANNEX B.

| content | mg/kg | | |

Table 6: Data sets on ERM-CC015a received from the participating laboratories

Laboratory	Sample A			Sample B					
	# 1	# 2	# 3	# 4	# 5	# 6	mean	sd	rsd
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	%
L01	1980	1999	1976	2006	1975	1957	**1982**	18	0,9
L02	2108	2100	2188	2074	2103	1880	**2076**	103	5,0
L03	1846	1998	1980	1892	1952	1918	**1931**	57	3,0
L04	1663	1709	1657	1737	1642	1661	**1678**	37	2,2
L05	2444	2424	2338	2302	2310	2366	**2364**	59	2,5
L06	1840	1820	1870	1930	2010	2140	**1935**	122	6,3
L07	1828	1828	1794	1779	1823	1898	**1825**	41	2,2
L08	2003	1948	2061	1969	2078	1956	**2003**	55	2,8
L09	1474	1494	1686	1416	1322	1540	**1489**	122	8,2
L10	1946	1963	1941	1907	1918	1966	**1940**	24	1,2
L11	1771	1723	1713	1744	1766	1692	**1735**	31	1,8
L12	2216	2201	2256	2046	2105	2118	**2157**	80	3,7

According to these results, the mean of laboratory means of 1886,36 mg/kg TPH was taken as the best estimate for the value to be certified, and the standard deviation of the mean of laboratory means of 57,77 mg/kg TPH as the uncertainty contribution from characterisation by intercomparison.

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/FDIS 16703:2003 having been quantified in relation to the certified calibration standard BAM-K10. Thus, the stated references for ERM-CC015a are ISO/FDIS 16703:2003 and the calibration standard BAM-K10 mentioned for this purpose therein.

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 from 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-K10 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 expansion 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 ERM CC015a

CRM	TPH content in mg/kg		
	Certified value, corrected for purity	Uncertainty of the certified value	Expanded uncertainty of the certified value
ERM CC015a	**1820**	**65**	**130**

6 Information on the proper use of ERM-CC015a

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 as mentioned in ISO/FDIS 16703:2003.

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 weight. 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 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 Federal Institute for Materials Research and Testing (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

[1] ISO/FDIS 16703:2003. Soil Quality - Determination of hydrocarbon content in the range of C_{10} to C_{40} by gas chromatography

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

[3] DIN EN 14039:2000. Waste – Determination of hydrocarbon content in the range of C_{10} - 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] C. Löser, A. Zehnsdorf, M. Fussy, P. Morgenstern. Möglichkeiten zur Kostenreduzierung bei der Entsorgung Schwermetall-kontaminierter Flusssedimente – ein Fallbeispiel. *Altlasten spektrum* (2001) 1, 18 – 27

[6] A.M.H. van der Veen, D.A.G. Nater. Sample preparation from bulk samples: An overview. *Fuel Processing Technology* (1993) **36**, 1 – 7

[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] Guide To The Expression Of Uncertainty In Measurement. ISO, Geneva (1993). (ISBN 92-67-10188-9) (Reprinted 1995)

[9] ISO Guide 35 (Final draft), ISO/REMCO, April 2005

[10] For detailed information on the ERM agreement see: www.erm-crm.org/ermcrm

[11] 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. 10 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/FDIS 16703:2003 ☐ ja ☐ nein

Clean-up gemäß ISO/FDIS 16703:2003 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 K-010 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/FDIS 16703:2003, Pkt. 9.4.2 (in %): ☐

Results for the control solutions (TPH content initially unknown to the participants)

Laboratory		Solution 1				Solution 2				Calibration					number
		# 1	# 2	mean	sd	# 1	# 2	mean	sd	low	high	blank 1	blank 2	rec.	of
												mg kg^{-1}	mg kg^{-1}	in %	pts.
L01	mg ml^{-1}	0,710	0,715	**0,713**	0,00354	1,632	1,629	**1,631**	0,00212	0,509	4,099	0	0	81,0	5
	counts	6.803.590	6.848.820	**6.826.205**	31982,4	14.599.700	14.572.900	**14.586.300**	18950,5	5.063.180	35.373.700				
L02	mg ml^{-1}	0,670	0,667	**0,669**	0,00212	1,490	1,510	**1,500**	0,01414	0,050	1,500	0	0	101,5	7
	counts	536	530	**533**	4,2	1.180	1.190	**1.185**	7,1	54	1.211				
L03	mg ml^{-1}	0,741	0,742	**0,742**	0,00071	1,683	1,679	**1,681**	0,00283	0,160	3,200	66	56	94,7	7
	counts	26.520	26.570	**26.545**	35,4	61.228	61.073	**61.151**	109,6	5.347	117.150				
L04	mg ml^{-1}	0,685	0,697	**0,691**	0,00849	1,565	1,596	**1,581**	0,02192	0,524	4,156	70	54	79,9	5
	counts	168.868.800	171.802.500	**170.335.650**	2074439,2	390.992.100	398.887.800	**394.939.950**	5583103,0	128.124.100	1.043.341.000				
L05	mg ml^{-1}	0,508	0,527	**0,518**	0,01344	1,43	1,25	**1,340**	0,12728	0,096	1,434	< 20	< 20	85,0	6
	counts	919.609	945.609	**932.609**	18384,8	2.197.662	1.951.512	**2.074.587**	174054,3	345.555	2.113.160				
L06	mg ml^{-1}	0,696	0,691	**0,694**	0,00354	1,62	1,63	**1,625**	0,00707	0,100	5,000	< 50	< 50	87,0	6
	counts	43.789	43.424	**43.607**	258,1	101.396	101.447	**101.422**	36,1	4.320	304.000				
L07	mg ml^{-1}	0,72	0,721	**0,721**	0,00071	1,604	1,61	**1,607**	0,00424	0,504	4,028	27	24	80,8	8
	counts	49.465	49.551	**49.508**	60,8	99.377	99.699	**99.538**	227,7	37.849	236.537				
L08	mg ml^{-1}	0,701	0,713	**0,707**	0,00849	1,595	1,612	**1,604**	0,01202	0,050	5,000	13	9	96,7	5
	counts	60.249	61.498	**60.874**	883,2	135.818	137.247	**136.533**	1010,5	7.100	445.660				
L09	mg ml^{-1}	0,702	0,686	**0,694**	0,01131	1,66	1,65	**1,655**	0,00707	0,200	2,000	0	0	100,0	7
	counts	7.246.808	7.085.361	**7.166.085**	114160,3	17.171.448	17.063.757	**17.117.603**	76149,0	2.128.769	20.983.654				
L10	mg ml^{-1}	0,683	0,677	**0,680**	0,00424	1,64	1,66	**1,650**	0,01414	0,400	2,000	0	0	95,0	5
	counts	41.200	41.100	**41.150**	70,7	98.500	101.000	**99.750**	1767,8	24.000	120.000				
L11	mg ml^{-1}	0,77	0,779	**0,775**	0,00636	1,72	1,716	**1,718**	0,00283	0,100	5,000	3	8	96,0	5
	counts	20.013.718	20.247.638	**20.130.678**	165406,4	44.527.352	44.445.248	**44.486.300**	58056,3	3.339.700	142.500.944				
L12	mg ml^{-1}	0,787	0,797	**0,792**	0,00707	1,762	1,732	**1,747**	0,02121	0,050	2,500	0	0	80,0	11
	counts	5.784.000	5.899.000	**5.841.500**	81317,3	12.554.000	12.344.000	**12.449.000**	148492,4	583.000	17.110.000				
			Mean:	0,699	mg kg^{-1}		Mean:	1,611	mg kg^{-1}						
			Gravimetry:	0,713	mg kg^{-1}		Gravimetry:	1,619	mg kg^{-1}						

sd: Standard deviation

blank: Procedural blank

rec: Recovery of calibration standard (according to ISO/FDIS 16703)

ANNEX C:

Results of the homogeneity study on ERM-CC015a. SD – Standard deviation. RSD – Relative standard deviation.

Sample	Replicate determination							
No.	**1** [mg kg^{-1}]	**2** [mg kg^{-1}]	**3** [mg kg^{-1}]	**4** [mg kg^{-1}]	**5** [mg kg^{-1}]	**Mean** [mg kg^{-1}]	**SD** [mg kg^{-1}]	**RSD** [%]
6	1801,25	1750,58	1772,00	1749,87	1704,78	1755,70	35,33	2,01
30	1826,65	1761,25	1846,45	1751,79	1802,77	1797,78	40,86	2,27
54	1846,47	1796,72	1764,27	1664,69	1817,49	1777,93	70,04	3,94
78	2023,06	1852,79	1837,55	1894,06	1532,78	1828,05	180,47	9,87
102	1922,80	1776,96	1633,79	1636,38	1735,20	1741,03	119,18	6,85
126	1996,23	1871,81	1814,78	1738,22	1696,91	1823,59	117,84	6,46
150	2076,18	1805,96		1879,05	1753,19	1878,60	141,47	7,53
174	1752,21	1608,70	1723,86	1955,10	1613,49	1730,67	140,97	8,15
198	1749,23	1730,87	1726,15	1651,56	1717,50	1715,06	37,35	2,18
222	1752,87	1779,81	1873,94	2023,61	1792,03	1844,45	109,87	5,96
246	1833,37	1872,07	1711,35	1969,26	1806,62	1838,53	94,12	5,12
270	1593,17	1670,17	1735,20	1766,66	1568,72	1666,78	86,17	5,17
294	1773,76	1803,32	1652,95	1781,38	1758,44	1753,97	58,74	3,35
318	1951,64	1794,03	1612,86	1865,86	1753,95	1795,67	126,90	7,07
342	1854,81	1724,86	1543,92	1932,27	1766,25	1764,42	147,08	8,34

ANOVA (5 g Einwaage)

Streuungs-ursache	*Quadrat-summen (SS)*	*Freiheits-grade (df)*	*Mittlere Quadrat-summe (MS)*	*Prüfgröße (F)*	*P-Wert*	*kritischer F-Wert*
Zwischen den Gruppen	213129,29	14	15223,52	1,2882	0,24211	1,8632
Innerhalb der Gruppen	697204,5	59	11817,03			
Gesamt	910333,79	73				

The uncertainty between bottles u_{bb} (= S_{bb}) is calculated according to (1) and amounts to 26,10 mg/kg.

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

Results of the initial stability study on ERM-CC015a.

+4°C

1 Month	TPH [mg/kg]	3 Months	TPH [mg/kg]	6 Months	TPH [mg/kg]
37-1	2047,38	**38-1**	2123,81	**39-1**	1822,21
37-2	2023,01	**38-2**	1834,73	**39-2**	2102,96
37-3	1963,96	**38-3**	2013,33	**39-3**	2166,49
37-4	1972,72	**38-4**	1956,56	**39-4**	2125,99
Mean	2001,77		1982,1075		2054,41
SD	34,66		104,20		135,98

+20°C

1 Month	TPH [mg/kg]	3 Months	TPH [mg/kg]	6 Months	TPH [mg/kg]
65-1	2195,45	**66-1**	2004,75	**67-1**	2014,21
65-2	1848,26	**66-2**	2026,11	**67-2**	1989,31
65-3	1915,21	**66-3**	1915,21	**67-3**	1955,17
65-4	2019,1	**66-4**	1902,79	**67-4**	1914,93
Mean	1994,505		1962,215		1968,405
SD	131,01		53,93		37,32

+40°C

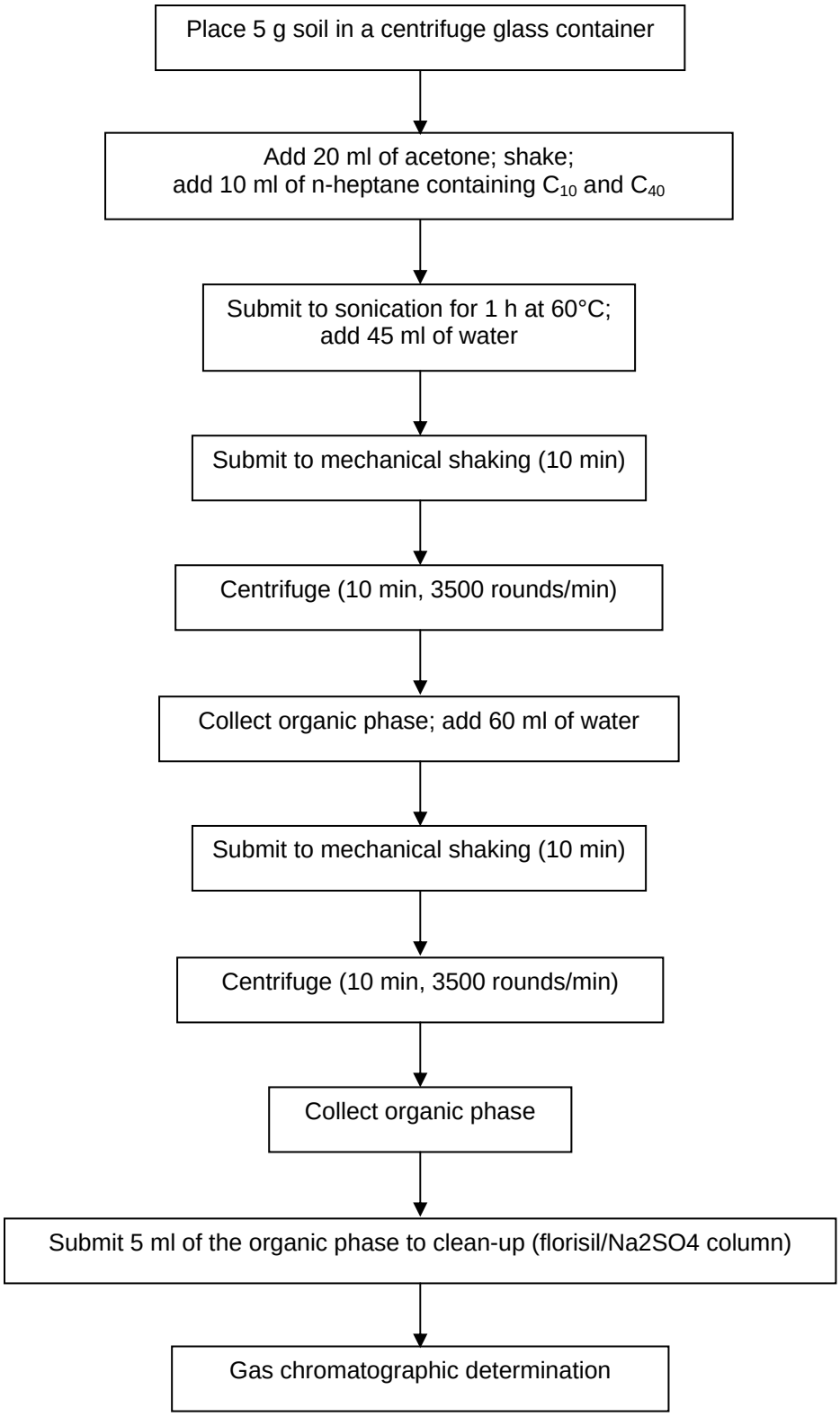
1 Month	TPH [mg/kg]	3 Months	TPH [mg/kg]	6 Months	TPH [mg/kg]
44-1	2136,82	**45-1**	1945,0	**46-1**	1872,70
44-2	1969,35	**45-2**	1875,3	**46-2**	1969,35
44-3	1778,28	**45-3**	1830,8	**46-3**	1778,28
44-4	1704,77	**45-4**	1828,9	**46-4**	1704,77
Mean	1897,305		1870,0		1831,28
SD	168,67		47,1027013		99,49

+ 60°C

0,5 Month	TPH [mg/kg]	1 Month	TPH [mg/kg]
42-1	1950,11	**43-1**	1874,62
42-2	1911,16	**43-2**	1843,34
42-3	1679,10	**43-3**	1834,67
42-4	1780,60	**43-4**	1632,77
Mean	1830,24		1796,35
SD	107,50		95,60

- 20°C

6 Months	TPH [mg/kg]	6 Months	TPH [mg/kg]	6 Months	TPH [mg/kg]
88-1	2061,27	**212-1**	2102,76	**338-1**	1969,29
88-2	1796,02	**212-2**	1814,83	**338-2**	1993,91
88-3	1734,08	**212-3**	1881,95	**338-3**	1822,11
88-4	2009,63	**212-4**	1986,85	**338-4**	1848,89
Mean	1900,25		1946,5975		1908,55
SD	138,17		109,03		74,17

ANNEX D:

Outline of the analytical procedure used for homogeneity and stability studies