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ERM-CC017: Mineral oil contaminated soil

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 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 (CRM). CRM based on sediment [5] and waste [6].had been developed in past few years and have been on sale since then: ERM-CC015a (sediment) and ERM-CC016 (waste).

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, 2 and 3] which are harmonized meanwhile. Thus, TPH is a parameter necessarily to be defined by the method which has strictly to be followed. The reference material ERM-CC017 is meant to be used for the verification of the quantification of TPH according to ISO 16703:2004 (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” soil substrate and characterised with regard to homogeneity and stability of the TPH content. A total of ten 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.

2 Production of the candidate material

2.1 Selection of the starting material

The sandy soil material was sampled at a soil decontamination plant in Berlin from a large heap of contaminated soil debris excavated from a former industrial site immediately before starting there a biodegradation process of mineral oil (TPH) content by microbial activity [7]. Based on field analyses of this debris the degree of contamination was as high as needed for our purpose.

2.2 Preparation of the candidate material

Sampling was done by means of a sieve with 8 mm aperture to remove large mineral and biologic matter from the bulk of approximately 180 kg of wet soil taken for CRM preparation. Thereafter the material was air-dried to constant weight before further processing. After drying, the bulk material (ca. 140 kg) was passed through a pin mill to gently smash the brittle agglomerates contained in the material. After classification by means of an automatic sieving station a total amount of 24.2 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 moved in a drum hoop mixer (J. Engelsmann AG, Ludwigshafen; Germany) for approx. 24 h total). Further homogenisation and bottling was achieved using a VIS type mixer (AMK, Aachen, Germany) where the mixing trough with a helically shaped mixing blade 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 289 units were bottled in 125 mL amber screw-capped glass bottles containing (81.4 ± 0.1) g and units were numbered in the order of leaving the bottling process. The screw caps equipped with Teflon inserts were tightly closed and sealed with shrinking foil. All units were stored at -20 °C directly after bottling. Table 1 comprises the chemical and physical characterisation of the matrix of the candidate material. The water content of soil is at equilibrium with the ambient atmosphere under typical laboratory conditions.

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 16703:2004. 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
60°C (5 min) → 360°C (15 min)
Heating rate: 40°C/min
Injection volume: 3µL
Detector temperature: 370°C

Example for a set of calibration solutions			
cal 1:	0.4989 mg/mL	cal 5:	2.0327 mg/mL
cal 2:	0.7342 mg/mL	cal 6:	2.4849 mg/mL
cal 3:	0.9831 mg/mL	cal 7:	2.9889 mg/mL
cal 4:	1.4689 mg/mL	cal 8:	4.0074 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-CC017

Measurand	**Value**	**Method**
Particle size range	0 – 125 µm	Sieving
Water content	(1.62 ± 0.03) %	*Karl-Fischer*-Titration
Drying loss	(1.89 ± 0.08) %	Gravimetry after drying to constant weight at 105°C (DIN ISO 11465)
Total organic carbon	(44.8 ± 0.4) mg/g	DIN ISO 10694
Total inorganic carbon	(6.3 ± 0.3) mg/g	DIN ISO 10694
CHN-Analysis	C: (5.62 ± 0.05)%; H: (0.693 ± 0.014)%; N: (0.192 ± 0.009)%	Combustion
pH	7.83 ± 0.10	E DIN ISO 10390

Table 1 comprises the chemical characterisation of the matrix of the candidate material. The relatively high water content is at equilibrium with the atmosphere under typical laboratory conditions and corresponds to the relatively 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 9.4 of ISO standard along with the a chromatogram of the employed calibration standard. The mineral oil pattern in this soil fraction seems to be typical for this type of matrix with an aged contamination. as it has been observed similarly before in comparable soil samples prepared for recent PT rounds of BAM. 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 16703:2004 and available from BAM: (www.webshop.bam.de)

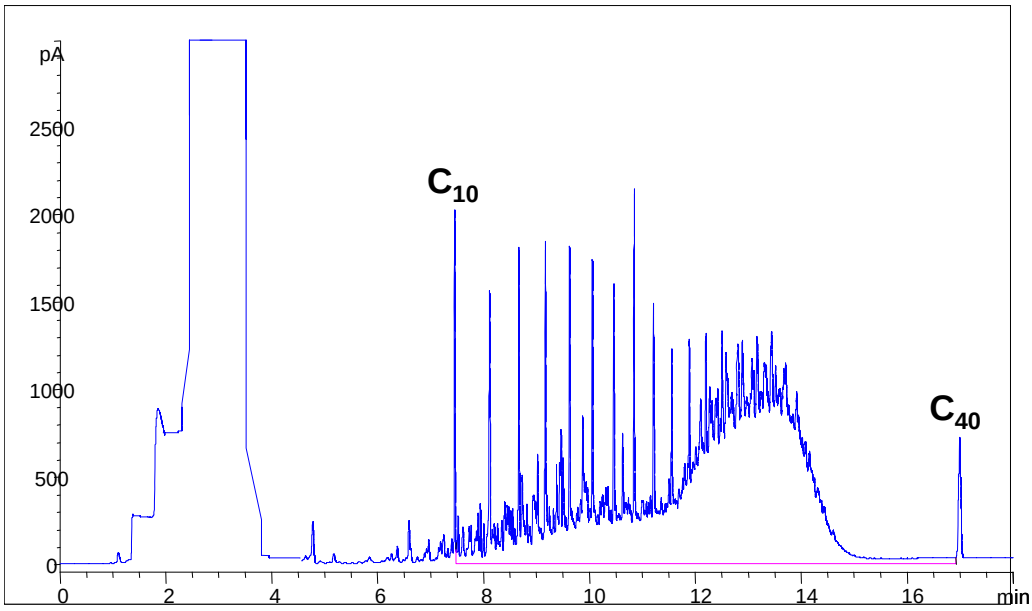


Fig. 2a: Chromatogram of the calibration standard BAM-K10

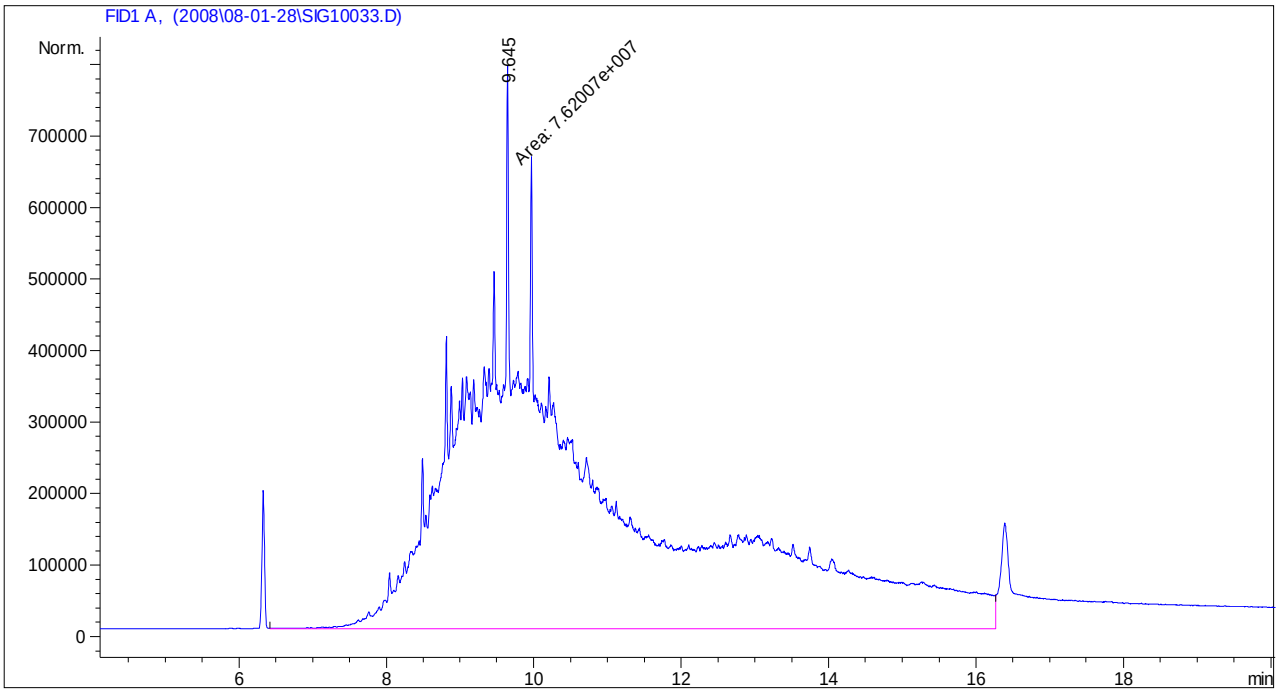


Fig. 2b: Chromatogram of an extract of ERM-CC017 according to ISO 16703:2004

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

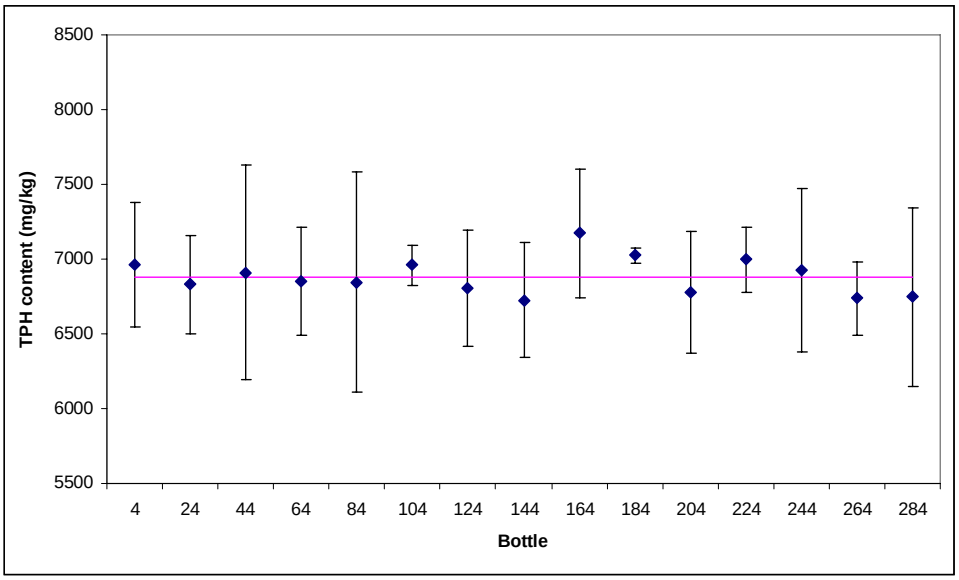


Fig. 3: Results of the homogeneity study (means and standard deviations); Mean of all determinations: 6884 mg/kg

15 units were selected equidistantly from the whole set of 289 bottles. They were analysed three times each according to ISO 16703:2004 using a sample intake of 5 g (for details of the method see ANNEX D).. All 15 units were extracted once under repeatability conditions on three consecutive days. Processed extracts were analysed by GC-FID under repeatability conditions in that all 45 extracts were quantified against one calibration after randomisation. The results are given in Fig. 3 and the individual data and the analysis of variance are collected in 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 133.84 mg/kg for 5 g sample intake using formula (1) according to ISO Guide 35 [8].

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

S_{method} = Method variability ($= \sqrt{MS_{within}}$)
n = Number of replicate determinations
N = Number of bottles analysed

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 [9] accelerated ageing at temperatures between 4 and 60°C over periods of 4 weeks to 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 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
1	125	132	140		initial study
2				118	initial study
3	126	133	141		initial study
4				122	initial study
6	127	134	142	123	initial study
12	128	135	143		initial study
24	129	136			1)
36	130	137			1)
48	131	138			1)
60		139			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 six extracts obtained from two reference samples evenly distributed over the whole measurement sequence were measured together with the exposed samples. A slight however 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).

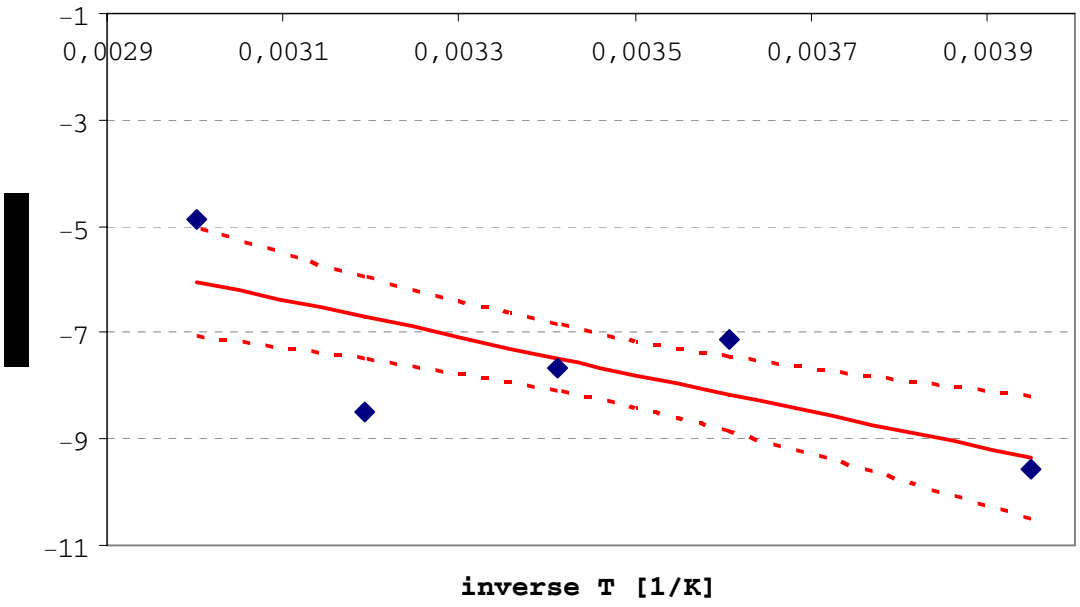


Fig. 4: Reaction rate for TPH in dependence on the inverse temperature (semi-logarithmic plot)

As can be seen from the plot, the temperature dependence can roughly 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 of ΔE is 28.9 kJ/mol is relatively small compared to similar materials. 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 results are given in table 5.

Table 5: Estimation of shelf life (time after which the certified value falls out of U)

temp °C	Months	Years
-20	285	23.7
4	136	11.3
20	74	6.2
40	30	2.5
60	12	1.0

Although shelf life at a storage temperature of -20°C is quite considerable, any exposure to room or even higher temperatures may reduce the time of validity of ERM-CC017. 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.

As can be seen from fig. 4, the dependence of the observed degradation rate on temperature is merely described by the assumed model. Most problematic are the results obtained for 4°C and 40°C. Although instrument effects are suspected to having caused these deviations, for compensation an additional contribution u_{lts} to the overall uncertainty of the certified value was derived from the time dependencies of the analyte content, again in a worst-case scenario.

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-CC017 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 nine field laboratories were selected on grounds of a good performance in several 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 16703:2004 and the declaration of commitment to comply with these requirements during the certification analyses. However, only eight of these laboratories delivered their results to BAM. Additionally, two experienced laboratories of ERM partners LGC and BAM took part in this exercise. Thus ten data sets were evaluated at the end.

5.2 Design of the study

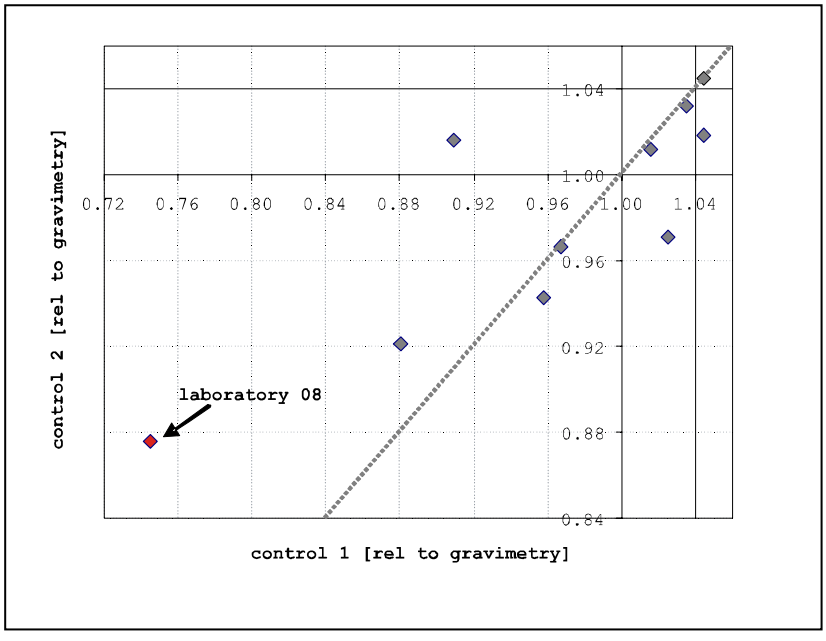
Two units of the candidate material were to be analysed by each laboratory in triple. The information that the level of content was to be expected between 3000 and 9000 mg/kg was provided as well as certified calibration standard BAM-K10 to ensure equal conditions as far as technically feasible (see 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-K010 such that they correspond to the lower and upper region of the calibration range. The standard procedure according to ISO 16703:2004 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. Table 6 contains the results as received from the participating laboratories.

Table 6: Data sets on ERM-CC017 received from the participating laboratories

Laboratory	Sample A			Sample B					
	# 1	# 2	# 3	# 4	# 5	# 6	mean	sd	rsd
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%
C01	7341	7384	7412	7095	7413	7527	7362	118.1	1.60
C03	6300	6350	6570	6430	6340	6660	6442	117.2	1.82
C04	6240	6380	6260	6110	6430	6040	6243	122.7	1.97
C05	7497	7800	7683	7264	7441	7374	7510	162.5	2.16
C06	7543	7558	7636	7199	6943	6917	7299	264.0	3.62
C07	6321	6186	6832	6003	5976	5982	6217	270.6	4.35
C08	7480	7220	7600	6770	6790	7470	7222	297.1	4.11
C09	7090	7121	6912	6800	6558	6559	6840	202.1	2.95
C10	7028	6242	5946	5902	5740	6116	6162	374.3	6.07
C11	6698	6988	7039	7411	7505	7528	7195	275.3	3.83



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.

Fig. 5: Plot of the mean values found by the laboratories for control solutions 1 and 2 normalised to gravimetric contents

For each laboratory, the mean laboratory value determined for the sample was plotted against the recovery the laboratory attained for the control solutions. Figure 5 shows the plot of the results for the two control solutions against each other. As can be seen from the graph, 9 out of 10 laboratories group around the centre (formed by a recovery of unity and the mean of laboratory means of the intercomparison). Some of the laboratories out of this group show positive others show slightly negative correlation between the sample and the control value. Only one laboratory (lab number 08, highlighted) is distant from the main group, and additionally shows a large anti-correlation between sample and control value.

Although no further investigation into the reasons for this discrepancy have been conducted, it seems justifiable to exclude, for technical reasons, the sample value of this particular laboratory from further processing.

Table 7: Results of the statistical evaluation of the data from table 6

	Mean	SD	u(x)	CI	Pooling Data sets	Scheffé	Bartlett	outlier 0.01(0.05)				Gauss	Skew/Kurto	**certify**
	mg/kg	mg/kg	mg/kg	mg/kg			(0.01)	Cochran (0.01)	Grubbs E	Grubbs D	Nalimov (0.01)			
with Lab 08	6849	534	168,87	382	no	10	no	hom	-(-)	-(-)	-(-)	yes	yes	yes
without Lab 08	6808	549	183	422	no	9	no	hom	-(-)	-(-)	-(-)	yes	yes	yes

5.3.2 Statistical evaluation

The data set as shown in table 6 after removal of laboratory 08 for technical reasons was used for further statistical processing.

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 SD of the distribution of laboratory means, and the standard deviation of the mean of laboratory means
- the confidence interval CI 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 results of the above calculations and tests for a data evaluation based upon the laboratory means are given in the table on the left. 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: No outliers detected (significance level 0.05 and 0.01).
- *Dixon*-, *Grubbs*- und *Nalimov*-Test: Laboratory means do not contain outliers (significance level 0.01).
- *Kolmogorov-Smirnov* and skewness/kurtosis test: Based on the available data, the hypothesis of normality cannot be rejected.

According to these results, the mean of laboratory means of 6808 mg/kg TPH was taken as the best estimate for the value to be certified, and the standard uncertainty u(x) of 183 mg/kg TPH as the uncertainty contribution from characterisation u_{char} by intercomparison (table 7).

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 16703:2004 having been quantified in relation to the certified calibration standard BAM-K10. Thus, the stated references for ERM-CC017 are ISO 16703:2004 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 u_{com} must appropriately be composed from the uncertainty of characterisation u_{char}, the contribution from a possibly undetected inhomogeneity u_{bb}, the uncertainty of the purity correction u_{pur}, and according to

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

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, u_{bb} in clause 3, and u_{lts} in clause 4.1.
The final values obtained after rounding are given in table 8 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 of (1.62 ± 0.03) % (see table 1) was seen to remain stable if the material is handled according to the instructions in the certificate (see also clause 6).

Table 8: Certified TPH content of ERM CC017

CRM	TPH content in mg/kg		
	Certified value, corrected for purity	Uncertainty of the certified value	Expanded uncertainty of the certified value
ERM CC017	**6600**	**250**	**500**

6 Information on the proper use of ERM-CC017

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 16703.

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 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 16703:2004. 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

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[7] R. Margesin, A. Zimmerbauer, F. Schinner, Monitoring of bioremediation by soil biological activities, Chemosphere (2000) **40**, 339-346

[8] ISO Guide 35: Reference materials – General and statistical principles for certification Edition: 3, ISO/REMCO, Geneva 2006

[9] 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

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

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

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

ANNEX A: Result reporting sheet

Lab code:

Certification study:
TPH in soil

Remarks:
- Please make three single determinations per sample
- Please take care for using dimensions as requested and for assignment of data to the right sample number.

sample intake: ***(please weigh in approx. 5 grams respectively)***

Sediment		1	2	3
sample A	**g**			
	date			
sample B	**g**			
	date			

TPH contents:

Sediment		1	2	3
sample A	**mg/kg**			
	date			
sample B	**mg/kg**			
	date			

Only three significant figures should be reported

Control measurements:

		1	2
Procedure blank	**mg/kg**		
	date		

Unknown solutions No. 1 und 2 in n-heptane:
(both solutions already contain integration range markers n-decane und tetracontane)
(to be injected directly - no dilution required)

solution		1	2
solution No. 1	**mg/ml***		
	Counts		
	date		
solution No. 2	**mg/ml***		
	Counts		
	date		

Please report three significant figures !

Date: 2008 Signature: _____

ANNEX B: Methods reporting sheet

Name of Laboratory:

Please describe measurement conditions !

(Please mark applied option with a cross or inscribe details as required !)

TPH in soil

Sample preparation

Extraction method:

Duration [h]:

Extraction temperature [°C]: (by use of Soxhlet not required)

Extraction solvent: volume [ml]

When Soxhlet extraction applied: Capacity of extractor [ml]:

and: number of extraction cycles (estimated):

Procedure according to ISO 16703 ?

☐ yes ☐ no

Clean-up according to recommendations of ISO 16703 ? ☐ yes ☐ no

If no, please describe shortly:

GC parameters

Instrument type:

Detector: ☐ FID ***(definitely required!)***

column (dimensions, phase, etc):

Carrier gas/flow:

Injection method:

Injected volume [µl]:

Oven programme:

Integration: ☐ retention time range from C10 to C40 ***(definitely required!)***

External standard applied: ☐ BAM K-010 (gratis delivered by BAM)

Please describe dilution steps:

5 point calibration applied ? ☐ yes ☐ if no, number of calibration points (> 5)

(Minimum number required: 5 calibration points)

TPH calibration concentrations [mg/ml]:

Lowest calibration concentration: Counts

Highest calibration concentration: Counts

Please note: Dilution of solutions No. 1 and 2 which are ready for measurement is really not necessary!

Recovery according to ISO 16703, clause 9.4.2 (in %):

Annex C: Homogeneity and stability study, results

Results of the homogeneity study on ERM-CC017. The TPH content was determined using GC-FID according to ISO 16703 (see Annex D).

Bottle	Replicate determination, TPH content in mg kg^{-1}		
	1	2	3
4	6485	7174	7238
24	6502	6834	7153
44	6221	6858	7652
64	6606	6676	7267
84	6516	6332	7691
104	6843	6934	7106
124	6358	6963	7085
144	6542	6468	7164
164	6763	7625	7134
184		6988	7061
204	6489		7063
224	6895	7246	6853
244	6302	7306	7176
264	6517	6696	6999
284	6068	7190	6980

1-way Anova:

Bottle	*Replicates*	*Sum* (mg kg^{-1})	*Mean* (mg kg^{-1})	*Variance* (mg^2 kg^{-2})	*Standard deviation* (mg kg^{-1})
4	3	20896.97	6965.65667	174132.788	417.29
24	3	20489.29	6829.76333	105862.704	325.37
44	3	20730.76	6910.25333	513668.166	716.71
64	3	20548.84	6849.61333	131917.792	363.20
84	3	20539.21	6846.40333	543767.826	737.41
104	3	20882.93	6960.97667	17910.0462	133.83
124	3	20405.52	6801.84	151543.743	389.29
144	3	20173.72	6724.57333	146221.847	382.39
164	3	21522.13	7174.04333	186896.45	432.32
184	2	14049.543	7024.7715	2670.12396	51.67
204	2	13552.24	6776.12	164634.696	405.75
224	3	20994.41	6998.13667	46581.2936	215.83
244	3	20784.06	6928.02	298078.504	545.97
264	3	20211.04	6737.01333	59434.6558	243.79
284	3	20238.41	6746.13667	355713.424	596.42

ANOVA

Source of varaince	*Suqare sum (SS)* (mg^2 kg^{-2})	*Deegrees of freedom (df)*	*Mean square sum (MS)* (mg^2 kg^{-2})	*Testvalue (F)*	*P-Value*	*critical F-Value*
Between the bottles	634974.07	14	45355.29	0.23	1.00	2.06
Within the bottles	5630763.30	28	201098.69			
total	6265737.37	42				

Results of the initial stability study on ERM-CC017

+4°C

1 Month	TPH [mg/kg]	3 Months	TPH [mg/kg]	6 Months	TPH [mg/kg]	12 Months	TPH [mg/kg]
125-1	6834	**126-1**	6575	**127-1**	6697	**128-1**	6990
125-2	6736	**126-2**	6381	**127-2**	6841	**128-2**	7017
125-3	6990	**126-3**	6443	**127-3**	6335	**128-3**	6590
Mean	6853		6467		6624		6866
SD	128.21		99.39		260.50		238.85

+20°C

1 Month	TPH [mg/kg]	3 Months	TPH [mg/kg]	6 Months	TPH [mg/kg]	12 Months	TPH [mg/kg]
132-1	7012	**133-1**	6761	**134-1**	7044	**135-1**	6994
132-2	6952	**133-2**	6722	**134-2**	6636	**135-2**	6573
132-3	6629	**133-3**	6500	**134-3**	6908	**135-3**	7160
Mean	6864		6661		6863		6909
SD	205.90		141.07		208.26		297.99

+40°C

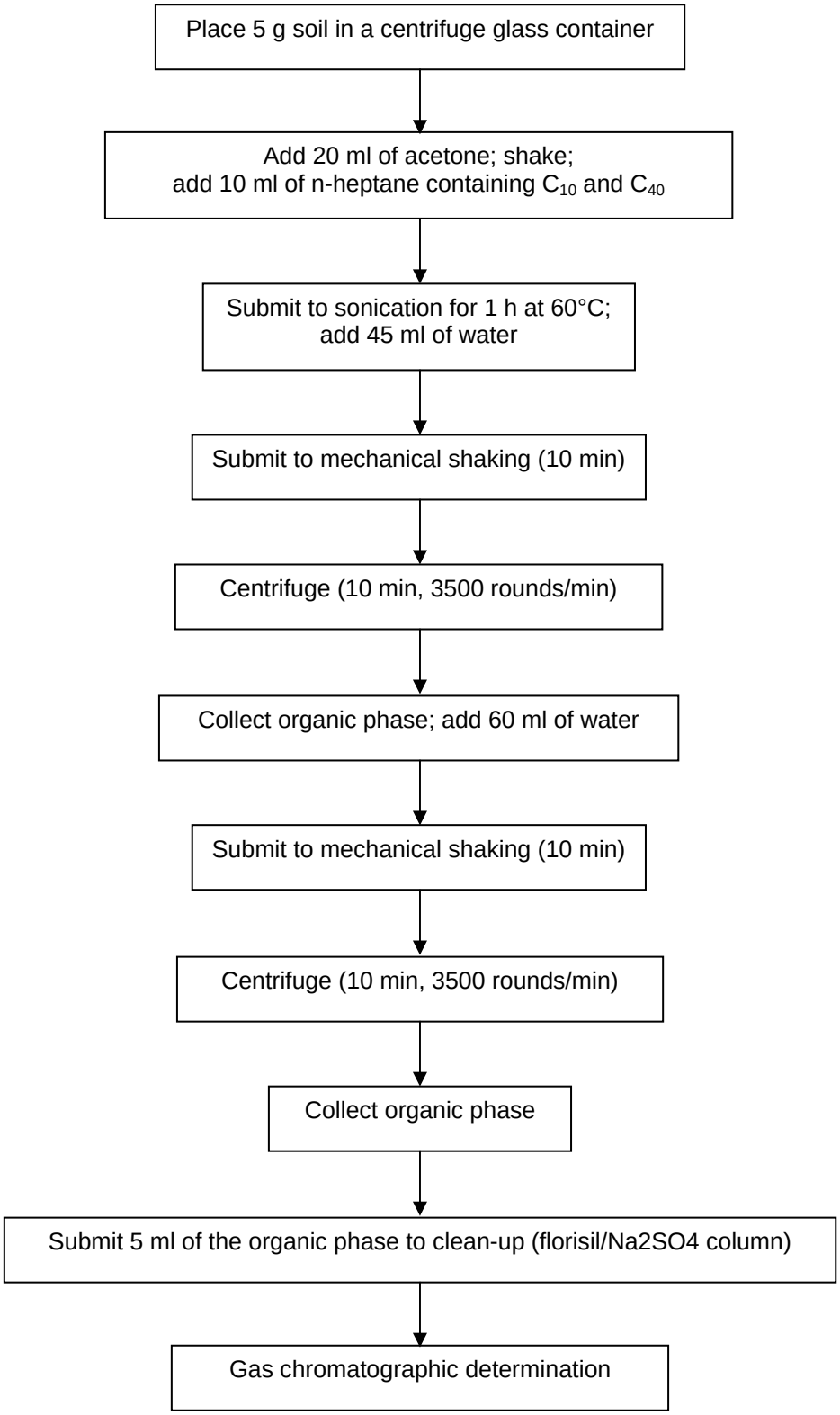
1 Month	TPH [mg/kg]	3 Months	TPH [mg/kg]	6 Months	TPH [mg/kg]	12 Months	TPH [mg/kg]
140-1	6885	**141-1**	7094	**142-1**	6838	**143-1**	6972
140-2	6936	**141-2**	6483	**142-2**	7066	**143-2**	6718
140-3	6953	**141-3**	6161	**142-3**	6876	**143-3**	6853
Mean	6925		6580		6926		6848
SD	35.48		473.96		121.98		127.04

+ 60°C

2 Months	TPH [mg/kg]	4 Months	TPH [mg/kg]	6 Months	TPH [mg/kg]
118-1	6828	**122-1**	6969	**123-1**	6877
118-2	6692	**122-2**	7000	**123-2**	6399
118-3	6535	**122-3**	6537	**123-3**	6330
Mean	6685		6836		6535
SD	146.66		258.68		297.86

- 20°C (reference)

	TPH [mg/kg]		TPH [mg/kg]
119-1	6996	**120-1**	6588
119-2	7039	**120-2**	6850
119-3	6632	**120-3**	6495
Mean	6889		6644
SD	223.72		183.98

ANNEX D:

Outline of the analytical procedure used for homogeneity and stability studies