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CERTIFICATION REPORT

The certification of the mass fraction of mineral oil hydrocarbons in solid waste

Certified Reference Material ERM®-CC016

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Certified Reference Material ERM®-CC016

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SUMMARY

This report describes the certification of a solid waste material intended for the determination of mineral oil hydrocarbons according to EN 14039 and ISO 16703. The preparation of the material is described, the results of the homogeneity and stability study are outlined, the measurement technique used and the results of the certification study are given.
The certified value and the uncertainty are:

Compound	Certified value	Uncertainty
	Mass fraction in mg kg^{-1}	
Mineral oil hydrocarbons	3010	± 220

The certified mass fraction represents the unweighted mean value of 13 laboratory means which were determined using the analytical methods described in EN 14039 and ISO 16703, respectively. The uncertainty represents the estimated expanded uncertainty U_{CRM} with a coverage factor of k = 2, corresponding to a level of confidence of about 95 % as defined in the Guide to the Expression of Uncertainty in Measurement, ISO (1993).

LIST OF ABBREVIATIONS AND SYMBOLS

ANOVA	Analysis of Variances
BAM	Federal Institute for Materials Research and Testing
b_p	Boiling point
CRM	Certified Reference Material
ERM	European Reference Material
FID	Flame ionization detector
GC	Gas chromatography
GUM	Guide to the Expression of Uncertainty in Measurement
IR	Infrared (spectroscopy)
ISO	International Organization of Standardization
RM	Reference Material
RSD	Relative standard deviation
SD	Standard deviation

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1 Introduction

The general term “mineral oil” comprises petroleum products with complex mixtures of hydrocarbons, ranging from motor gasoline, diesel- and heating oils, heavy fuel oils to lubricants. Due to the widespread use of mineral oils, these petroleum hydrocarbons are the most common organic contaminants to be found in soil and waste.
The gas chromatographic (GC) standard methods for the determination of mineral oil hydrocarbons in waste, soil and water [1, 2, 3] have been developed to replace the infrared (IR) spectroscopic methods, which are using Freon R 113 (1,1,2-Trichloro-1,2,2-trifluoroethane) as solvent.
Available reference materials on the basis of the former IR-method are losing importance because mineral oil is a parameter defined by a method which has strictly to be followed. The change from IR- to the new GC-methods is greatly facilitated by the availability of appropriate reference materials.
The intended use of the reference material ERM®-CC016 as internal quality standard allows the verification of the quantification of mineral oil hydrocarbons according to EN 14039:2004 in waste and closely related matrices such as soils according to ISO 16703:2004. Both standard methods are comparable.

The candidate material to be certified has been prepared at BAM as a mixture of “real-world” waste materials from different sources and characterised with regard to homogeneity and stability of the mineral oil content.
A total of 14 laboratories were selected on the basis of documented experience and proficiency and invited to participate in the certification study on this candidate material. Following internationally accepted procedures the certified mass fraction of mineral oil hydrocarbons, its uncertainty, the shelf life and the minimum amount for a single determination were evaluated.

2 Production of the candidate material

2.1 Selection and preparation of the starting materials

The term “waste” comprises a wide spectrum of possible matrices with complex compositions. Hence, it is difficult to define a representative waste reference material. However, typical areas of possible contaminations with mineral oil can be specified. Considerations were made to find out relevant waste compartments. On this basis the following three starting materials were selected:

The *building material* was contaminated with mineral oil as a consequence of an accident with a heating oil storage tank in 1997. The porous character of the building material (bricks) promotes the binding of mineral oil on the matrix. The gas chromatogram in figure A1 (ANNEX A) shows the boiling range of a typical heating oil. The open storage of this material at room temperature led to a (bio)degradation of the homologous chain of n-alkanes. But the typical diesel and heating oil compounds, pristane and phytane, are not degraded and still included in the GC chromatogram (visible as distinct peaks).

The *filter cake material* consists of residues from a nickel galvanic factory in Germany (low mineral oil contamination) and a chemical-physical waste treatment plant (high mineral oil contamination). The gas chromatogram (Fig. A2, ANNEX A) of the filter cake displays the high boiling range containing compounds with boiling points higher than 525°C (b_p of n-tetracontane $C_{40}H_{82}$).

A *marine sediment* sampled close to an offshore oil production platform in the North Sea is contaminated with mineral oil from drilling operations (Fig. A3, ANNEX A). The use of oil based drillmuds was banned in 1993. Olefinic-based mud is however still used for lubrication of the drillbit. Marine sediments tend to be contaminated with high boiling hydrocarbons, showing very low water solubility.

The single materials of *building material*, *filter cake* and *marine sediment* were already used in a feasibility study in the frame of the EU-project HYCREF (G6RD-CT-2002-00854-HYCREF) entitled “Certified Reference Materials for the determination of mineral oil hydrocarbons in water, soil and waste” (2003 – 2005). Remaining amounts of the well characterised single materials are the basis of this new reference material. The results of the HYCREF-project are outlined in the final technical report [4].

2.2 Preparation of the candidate material

The three starting materials were air dried to constant weight and then sieved. The sieve fraction < 500 µm was used for further preparation of the candidate reference material. The individual amounts of the starting materials and their corresponding mineral oil content are summarized in the following table.

Tab. 1: Starting materials used for preparation of ERM®-CC016

Starting material	Mass in kg	Mineral oil hydrocarbon content[1] in mg kg^{-1}	Dry matter content in %
Building material	9,629	2108	99,5
Filter cake	5,621	9177	86,4
Marine sediment	6,511	196	99,8

[1]) Results from the test-certification study in HYCREF-project (2004) based on the dry matter content

The material obtained after combining of the three starting materials (21,761 kg) was homogenised in a 30 L stainless steel barrel placed in a drum hoop mixer for 12 hours. It was decided not to conduct a further homogenisation step, e.g. cross-riffling, because the material was tested as not suitable for applying a cross-riffling scheme. Therefore, a total

number of 262 units were manually bottled in 100 mL amber glass bottles containing (83,0 ± 0,3) g sealed with screw caps with PTFE inserts and numbered in the order of leaving the bottling process. After bottling the whole batch was stored at -20°C.

2.3 Characterisation of matrix and analyte of candidate material

Table 2 contains the physical and chemical matrix composition of the candidate material representing the characteristics of the three starting materials according to the applied mass ratio of mixing.

Tab 2: Matrix characterisation of ERM®-CC016

Measurand	Value	Method
Particle size range	≤ 500 µm	Sieving
Water content	(3,95 ± 0,19) %	*Karl-Fischer*-Titration
Total organic carbon	(11,3 ± 0,4) g kg^{-1}	DIN ISO 10694
Total inorganic carbon	(2,7 ± 0,2) g kg^{-1}	DIN ISO 10694
Mass fraction of elements:		
w(C)	(13,3 ± 0,6) g kg^{-1}	CHN Elemental analysis
w(H)	(6,04 ± 0,23) g kg^{-1}	Catalytic combustion at 960°C
w(N)	(0,48 ± 0,01) g kg^{-1}	
pH (in water)	8,24 ± 0,02	E DIN ISO 10390

Figure 1 shows a typical chromatogram of an extract of the candidate material obtained with the procedure outlined in ANNEX B and analysed as mentioned in clause 2.4.

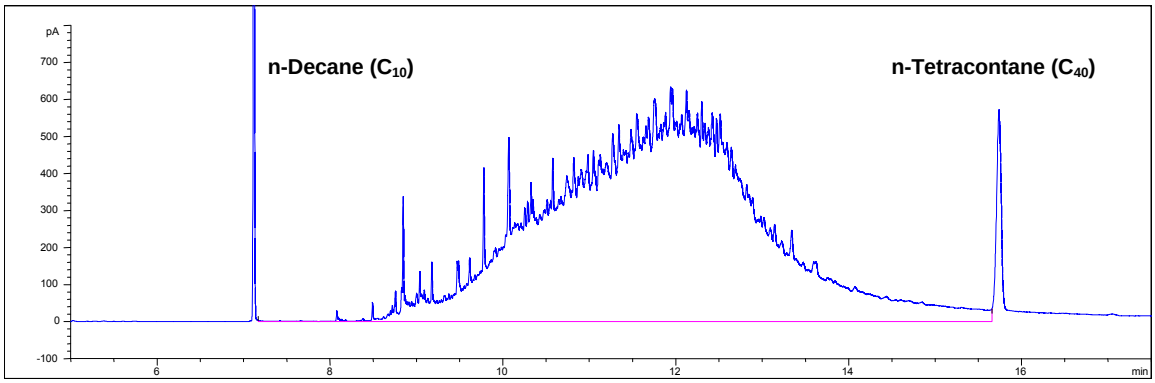


Fig. 1: GC FID chromatogram of an extract of candidate material

Characteristic features of this candidate material are the wide boiling range from b_p ~ 253°C (C_{14}) to b_p ~ 537°C (C_{42}), a maximum at b_p ~ 450°C (C_{30}) and the distinct peaks of pristine and phytane. As can be seen from the chromatograms of the three starting materials (ANNEX A), the *filter cake* contamination is the most dominating part of the candidate material and covers the mineral oil compounds contained in both *building material* and *marine sediment*.

2.4 Analytical method

The analytical method for the determination of mineral oil hydrocarbons in environmental matrices changed completely in the last couple of years. The infrared technique (IR) was replaced by a gas chromatographic method, which allows the quantification and (in some cases) the qualitative evaluation of the mineral oil composition.
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. Therefore, mineral oil hydrocarbons are quantified as a method defined sum parameter. For

this purpose a flame ionization detector is used, which yields signals proportional to the actual amount of C and H over a wide range of content.
The standard method further includes an extraction step using the solvent mixture acetone/heptane (2:1 *v/v*), two washing steps with water, and a clean-up with Florisil® in order to remove interfering polar substances from the extract. The integration range of the gas chromatogram is prescribed between the retention time markers n-decane (C_{10}, b_p 174°C) and n-tetracontane (C_{40}, b_p 525°C). The fraction 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-K010[1] (mixture of diesel oil and lubricating oil, 1:1 w/w) was used. For the measurements on the candidate material a BPX-5 capillary column (15 m x 0.32 mm x 1 µm) and the following instrumental conditions were employed.

Tab. 3: Gas chromatographic conditions

Parameter	GC-conditions
Oven program	60°C (5 min) ⟶ 360°C (5 min)
Heating rate	40 K min^{-1}
Injection	3 µL on-column
Detector	FID, 370°C
Carrier gas	Helium 5.0, 3 mL min^{-1}
Make-up gas	Helium 5.0, 45 mL min^{-1}

The sample preparation done for homogeneity and stability studies is outlined in ANNEX B. Here, minor changes regarding EN 14039 were applied: A reduced sample intake (5 g) was used instead of 20 g (EN 14039). The volumes of solvent were reduced in a way that the solid/liquid-ratio remained equal to EN 14039. In order to facilitate the time consuming washing, only one washing step with a larger volume of water (150 mL instead of 100 mL) was applied. These changes were only applied for homogeneity and stability studies. For the certification study no changes regarding EN 14039 were allowed.

2.5 Minimum sample size

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

For homogeneity study 11 units were selected equidistantly from the whole set of 262 bottles. They were analysed five times each according to EN 14039 (modified) using a sample intake of 5 g. Details of sample preparation and instrumental conditions are given in clause 2.4 and ANNEX B. All 11 units were extracted once under repeatability conditions on five consecutive days.
Processed extracts were analysed by GC-FID under repeatability conditions in that all 55 extracts were quantified against one calibration after randomisation.
The evaluation of the homogeneity study was done by Analysis of Variances (ANOVA). For the measurement data and ANOVA see ANNEX C.
No evidence suggesting a rejection of the hypothesis that the material is homogeneous was found. A contribution of the uncertainty of the mineral oil hydrocarbon content between the bottles (u_{bb}) to the overall uncertainty of the certified reference material was nevertheless

[1] Certified calibration standard BAM-K010 is mentioned for this purpose in EN 14039 and ISO 16703 and available from BAM: www.webshop.bam.de

derived from the ANOVA results. The value for u_{bb} was estimated as 39,6 mg/kg for 5 g sample intake.

4 Stability study

4.1 Initial stability study

Experience regarding the deterioration of mineral oil hydrocarbons in environmental matrices already exists but the specific degradation always depends on the type of mineral oil, matrix composition, moisture content, temperatures and microorganisms. The aim of the initial stability study was to investigate a temperature-driven deterioration of the mineral oil content of this material.
Selected units of the candidate material were submitted to accelerated ageing at temperatures between 4°C and 60°C over periods of 2,5 weeks to 12 months as shown in table 4 to perform a so-called isochronous stability study [5].

Tab. 4: Accelerated ageing of exposed samples

Ageing [months]	Bottle-No. / Storage temperature 4°C	20°C	40°C	60°C	Remark
0.5			091	206	Initial study
1	100	140	231	130	Initial study
3	248	157	183	020	Initial study
6	059	113	026		Initial study
12	011	172			[1])
24	253	051			[1])
36	070	214			[1])
48	222				[1])
60	150				[1])

[1]) post-certification monitoring

After the respective periods of time the exposed units were stored at -20°C. All 13 units were analysed for mineral oil hydrocarbons using the method described in clause 2.4 and ANNEX B under repeatability conditions together with 3 reference samples which had been kept at -20°C over the whole period of the initial stability study. Two independent extracts were obtained for each exposed sample and reference sample (total: 13x2 + 3x2 = 32 extracts). The extracts of the reference samples were evenly distributed over the whole measurement sequence and measured together with the exposed samples. For the individual data of the initial stability study see ANNEX D.

The first post-certification analysis after 12 months was also taken into account for the stability evaluation.

In order to obtain estimates for the thermal behaviour of the samples at the lower and especially at the storage temperature, an *Arrhenius* model is assumed for the dependence of the reaction rate k_eff(T) on temperature. A plot of the reaction rate k_eff(T) over the inverse temperature is given in figure 2.

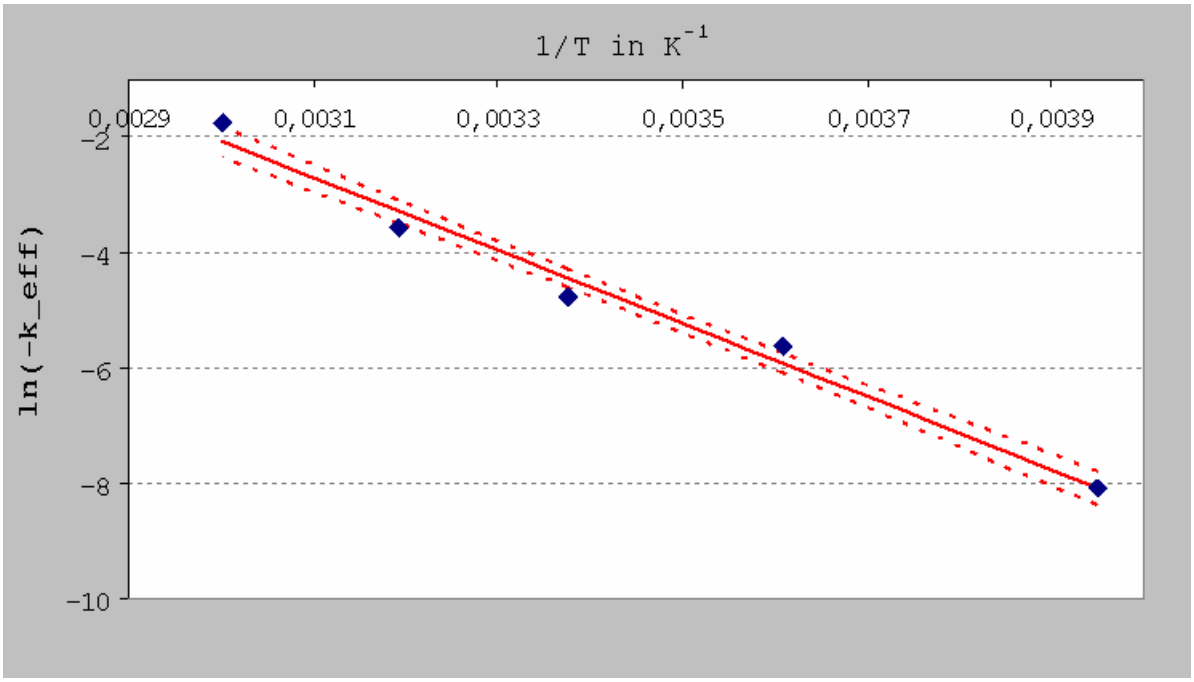


Fig. 2: Reaction rate for mineral oil hydrocarbons in dependence on the inverse temperature

As can be seen from the graph, the temperature dependence can indeed be approximated by a straight line. The corresponding confidence interval for the line is also given in the figure. The estimated activation energy ΔE is 52,56 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.

Tab. 5: Estimation of shelf life

Temperature °C	k_eff	Expiry (months)
-20	0,00042	**182,1**
4	0,00326	**23,5**
23	0,01382	**5,6**
40	0,04553	**1,7**
60	0,16311	**0,5**

The data table will be updating during post-certification monitoring. Although shelf life at a storage temperature of -20°C is quite considerable, any exposure to room or higher temperatures may reduce the time of validity of ERM®-CC016. 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 4.

5 Certification study

5.1 Participants

A total of 14 laboratories were invited to participate in the certification exercise. Six of these laboratories were selected due to a satisfactory performance in recent proficiency testing rounds on mineral oil analysis in soil operated by BAM and/or BAM-certification studies. Five laboratories were selected on grounds of their experience gained in the EU-project HYCREF dealing with mineral oil analysis in water, soil and waste. Additionally, three BAM laboratories (working groups/operators) took part in this certification study. The participants of the certification study are listed in table 6. Selection criteria for participants included the consistency of documentation of extraction, clean-up, calibration and instrumental analysis according to EN 14039 and the declaration of commitment to comply with these requirements during the certification analyses.

Tab. 6: Participants of the certification study “Mineral oil hydrocarbons in waste” in alphabetical order

Laboratory	City / Country
Alcontrol Specials	Hoogvliet, The Netherlands
Bundesanstalt für Materialforschung und –prüfung (BAM-I.21)	Berlin, Germany
Bundesanstalt für Materialforschung und –prüfung (BAM-I.22)	Berlin, Germany
Bundesanstalt für Materialforschung und –prüfung (BAM-I.23)	Berlin, Germany
Bundesanstalt für Geowissenschaften und Rohstoffe	Hannover, Germany
Chemlab GmbH	Bensheim, Germany
Dr. Kaiser & Dr. Woldmann GmbH	Hamburg, Germany
Dr. Ronald Fischer AUb Chemische Analytik- und Umweltberatung	Leinatal, Germany
Dr. Weßling Laboratorien GmbH	Altenberge, Germany
Estonian Environmental Research Centre (EERC)	Tallinn, Estonia
Landeslabor Brandenburg	Potsdam, Germany
Landesumweltamt NRW, Fachbereich 22 – Organische Chemie	Düsseldorf, Germany
Latvian Environment Geology and Metrology Agency (LEGMA)	Ūrmala, Latvia
Limnologisches Institut Dr. Nowak	Ottersberg, Germany

5.2 Design of the study

Two units of the candidate reference material were to be analysed by each laboratory in triple. In addition, each participant received two solutions of mineral oil in n-heptane with concentrations unknown to them. These control solutions were prepared gravimetrically from the certified calibration standard BAM-K010. The pure calibration standard BAM-K010 (mixture of diesel oil/lubricating oil 1:1 *w/w*) was provided to each participant to ensure equal conditions as far as technically feasible (see also clause 5.3.3). The standard procedure according to EN 14039 and ISO 16703 had to be followed strictly and was to be documented (see ANNEX E).
Results of the mineral oil content were to be reported in the so-called “Result reporting sheet” (ANNEX F) on the basis of sample intake. Results returned to BAM were scrutinised for consistency.

5.3 Evaluation of results and certified values

The results of the certification study were evaluated in accordance with ISO GUIDE 35 [6] and the specific requirements of the ERM agreement [7]. The computer software SoftCRM [8] 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 mineral oil concentration of the two control solutions directly by GC-FID measurement. In that way, the GC performance including calibration was tested. The individual results are listed in ANNEX G. For each laboratory, the normalised values of the GC control solution 1 and 2 were plotted against each other. Figure 3 shows the corresponding plot.

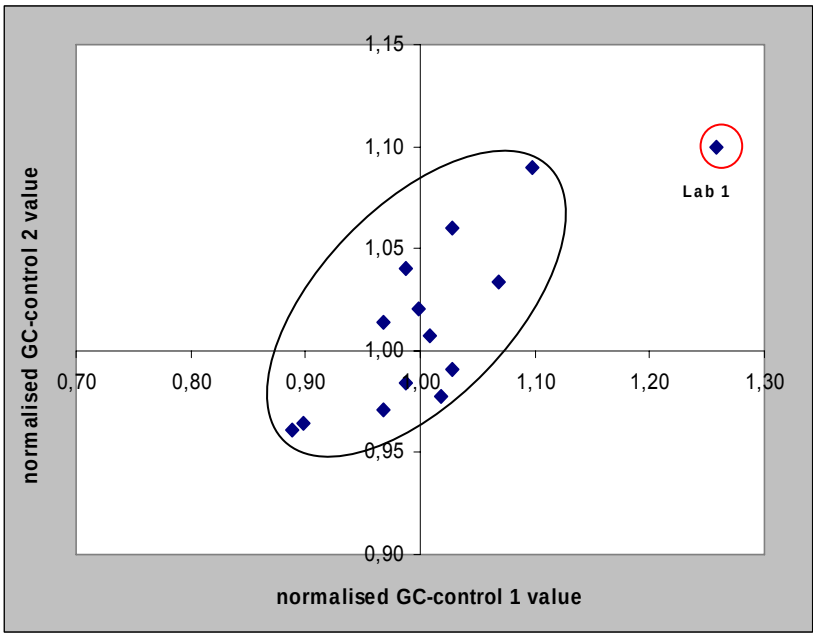


Fig. 3: Plot of the normalised values of GC-control solution 1 and 2 (normalised on the basis of the gravimetric values)

As can be seen from figure 3, 13 out of 14 laboratories group around the centre. Only one laboratory (Lab-No. 1, highlighted) is distant from the main group. The large positive correlation between both control values indicates a systematic calibration error.

The normalised sample (RM) value for each laboratory (normalised by the mean of laboratory means) was plotted against the mean of the normalised values determined for GC control solution 1 and 2. Figure 4 shows the corresponding plot.

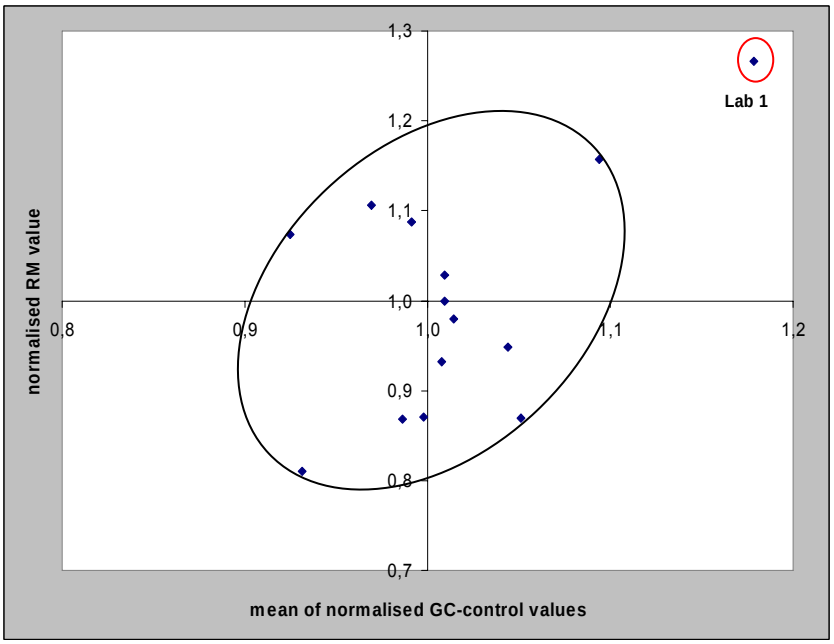


Fig. 4: Plot of lab's normalised sample values (normalised by the mean of laboratory means) against the mean of the normalised GC-control solutions 1 and 2

As can be seen from figure 4, 13 out of 14 laboratories group around the centre. Some of the laboratories out of this group show positive others negative correlation between the sample and the control value. Only one laboratory (Lab-No.1, highlighted) is distant from the main group. Assuming a calibration error of Lab-No.1 (see Fig. 3) the sample value would come closer to the main group after re-calibration. That means the sample preparation according to EN 14039 was done accurately but a systematic error in GC determination/calibration is mainly responsible for an unacceptable high result of the RM sample.
Investigations into the reasons for the discrepancy regarding the values of Lab-No.1 did not lead to a conclusion. Due to technical reasons (obvious GC problems/calibration) an exclusion of the sample value of laboratory No. 1 from further processing seems to be justifiable.

5.3.2 Statistical evaluation

After removal of laboratory No. 1 for technical reasons, the data set as shown in table 7 was used for further statistical processing.

Tab. 7: Accepted laboratory data sets

Laboratory	**Sample A**			**Sample B**					
	# 1 mg kg^{-1}	**# 2** mg kg^{-1}	**# 3** mg kg^{-1}	**# 1** mg kg^{-1}	**# 2** Mg kg^{-1}	**# 3** mg kg^{-1}	**Mean** mg kg^{-1}	**SD** mg kg^{-1}	**RSD** %
Lab 02	3110	3370	3420	3250	3710	3590	3408	219	6,4
Lab 03	3066	3039	3056	2944	2928	3030	3011	59	2,0
Lab 04	3283	3259	3269	3306	3203	3265	3264	34	1,1
Lab 05	3756	3613	3434	3789	3806	3638	3673	141	3,9
Lab 06	2980	3080	3130	3100	3170	3200	3110	77	2,5
Lab 07	2992	2986	2924	3000	2922	2926	2958	38	1,3
Lab 08	3231	3434	3402	3568	3542	3539	3453	127	3,7
Lab 09	2662	2788	2690	2672	2894	2853	2760	100	3,6
Lab 10	3525	3467	3516	3469	3598	3479	3509	50	1,4
Lab 11	3190	3216	3150	3138	3160	3180	3172	29	0,9
Lab 12	2690	2732	2724	2812	2812	2749	2753	49	1,8
Lab 13	2588	2651	2549	2575	2543	2518	2571	46	1,8
Lab 14	2810	2703	2677	2730	2884	2774	2763	76	2,8

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):

- *Scheffé*- and *Snedecor*-F-Test for identification of differences between data sets
- 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 table 8.

Tab. 8: Statistical parameters of the accepted data set

Mineral oil hydrocarbons in mg/kg							
Value	SD	u (x)	CI	TI	Data sets		Pooling
3108	342	95	207	1054	13		no
Scheffé	Bartlett	Outlier		α = 0,01 (0,05)		Gauss	Skew/Kurto
	α = 0,01	Cochran (0,01)	Grubbs E	Grubbs D	Nalimov	α = 0,01	
no	inhom	2(2,5,8)	-(-)	-(-)	-(-)	yes	yes

The main features are as follows:

- *Scheffé*- and *Snedecor*-F-Test: Data sets differ significantly.
- *Bartlett*-Test: Variances are inhomogeneous (at the significance level of 0,01).
- *Cochran*-Test: One outlier detected at a significance level of 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 the results outlined in table 8, the mean of laboratory means (w_{char}) of 3108 mg kg^{-1} mineral oil hydrocarbons was taken as the uncorrected (for purity) estimate for the value to be certified, and the standard deviation of the mean of laboratory means of 95 mg/kg mineral oil hydrocarbons as the uncertainty contribution from characterisation (u_{char}) by intercomparison.

5.3.3 Traceability

As pointed out, the mineral oil content is a parameter defined by the method employed for its determination. The certified value is then the mass fraction of mineral oil obtained by the analytical procedure according to EN 14039 (and ISO 16703) having been quantified in relation to the certified calibration standard BAM-K010. Thus, the stated references for ERM®-CC016 are EN 14039 / ISO 16703 and the calibration standard BAM-K010 mentioned for this purpose therein.

5.3.4 Certified value and combined uncertainty

The certified value w_{cert} (mineral oil hydrocarbon mass fraction) results from the estimate w_{char} of clause 5.3.2 corrected for the purity of the calibration standard f_{pur} (f_{pur} = 0,967) used in all of the experiments according to

$$w_{cert} = w_{char} \cdot f_{pur}$$

The corresponding combined uncertainty (u_{com}) is composed from the following contributions.

$$u_{com}^2 = u_{char}^2 + u_{preci}^2 + u_{bb}^2 + u_{pur}^2 + u_{rec}^2$$

In table 9 the individual terms of uncertainty are summarized.

Tab. 9: Contributions to the uncertainty of the mineral oil content of ERM®-CC016

Uncertainty contribution	Symbol	Value in mg kg^{-1}
Uncertainty of characterisation (standard deviation of the mean of lab means)	u_{char}	94,9
Uncertainty contribution due to precision data of participating labs	u_{preci}	13,6
Contribution from a possibly undetected inhomogeneity	u_{bb}	39,6
Uncertainty of the purity of used calibration standard	u_{pur}	28,0
Uncertainty of recovery from control solution measurement	u_{rec}	39,5

The certified values for the reference material are given in table 10 where the coverage factor for the expanded uncertainty is k = 2, corresponding to a level of confidence of about 95 %. The certified value and the expanded uncertainty are rounded according to the recommendations of GUM [9] 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).

Tab. 10: Certified mineral oil hydrocarbon content of ERM®-CC016

CRM	Mineral oil hydrocarbon mass fraction in mg kg^{-1}		
	Certified value w_{cert}, corrected for purity	Combined uncertainty of the certified value u_{com}	Expanded uncertainty of the certified value U_{CRM}
ERM®-CC016	**3010**	**110**	**220**

6 Information on the proper use of ERM®-CC016

6.1 Shelf life

From the initial stability study a preliminary shelf life of 15 years at a storage temperature not higher than -20°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 post-certification monitoring.

6.2 Transport, storage and use

The stability of the mineral oil content allows dispatch of the material at ambient temperature. However, customers are requested to report any deviating from nominal delivery times to the provider.
On receiving, the material has to be stored at -20°C in its original bottle. 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.

6.3 Safety instructions

The waste material was not sterilised, however, it is supposed to not exhibit any biological activity. 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] EN 14039, Characterization of waste – Determination of hydrocarbon content in the range of C_{10} to C_{40} by gas chromatography. 2004

[2] ISO 16703, Soil Quality - Determination of hydrocarbon content in the range of C_{10} to C_{40} by gas chromatography. 2004

[3] ISO 9377-2, Water quality - Determination of hydrocarbon oil index - Method using solvent extraction and gas chromatography. 2000

[4] EU-project HYCREF, Contract-No. G6RD-CT-2002-00854, Final Technical Report, May 2005

[5] 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

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

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

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

[9] Guide to the expression of uncertainty in measurement. ISO, Geneva (1993). (ISBN 92-67-10188-9) (Reprinted 1995)

8 Annexes

ANNEX A: GC-FID chromatograms of the starting materials

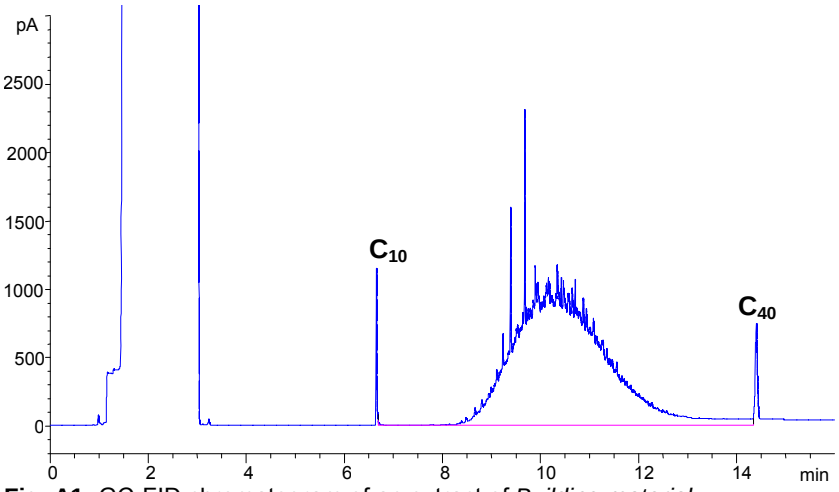


Fig. A1: GC-FID chromatogram of an extract of *Building material*

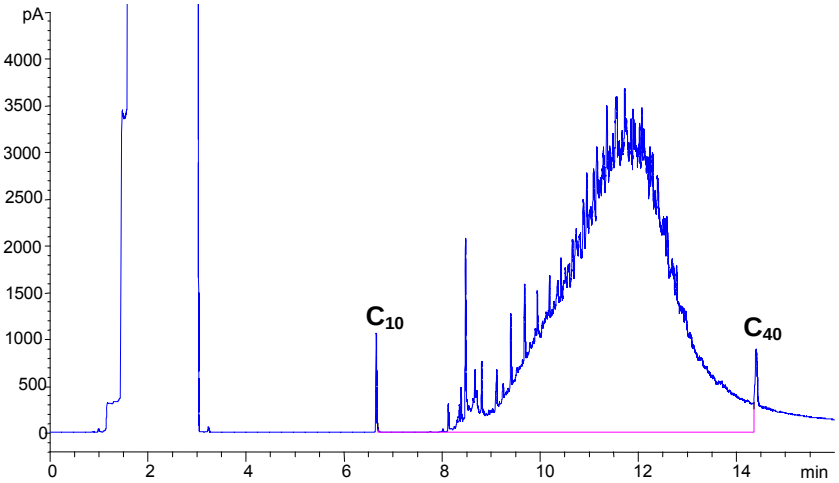


Fig. A2: GC-FID chromatogram of an extract of *Filter cake material*

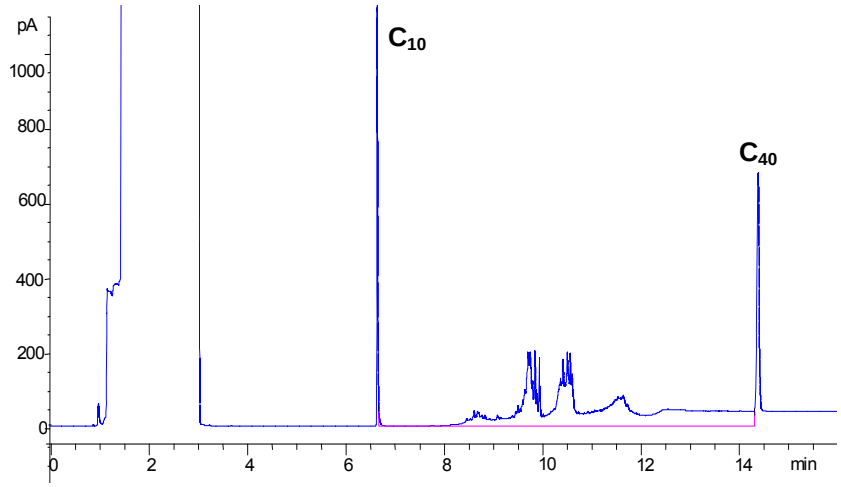
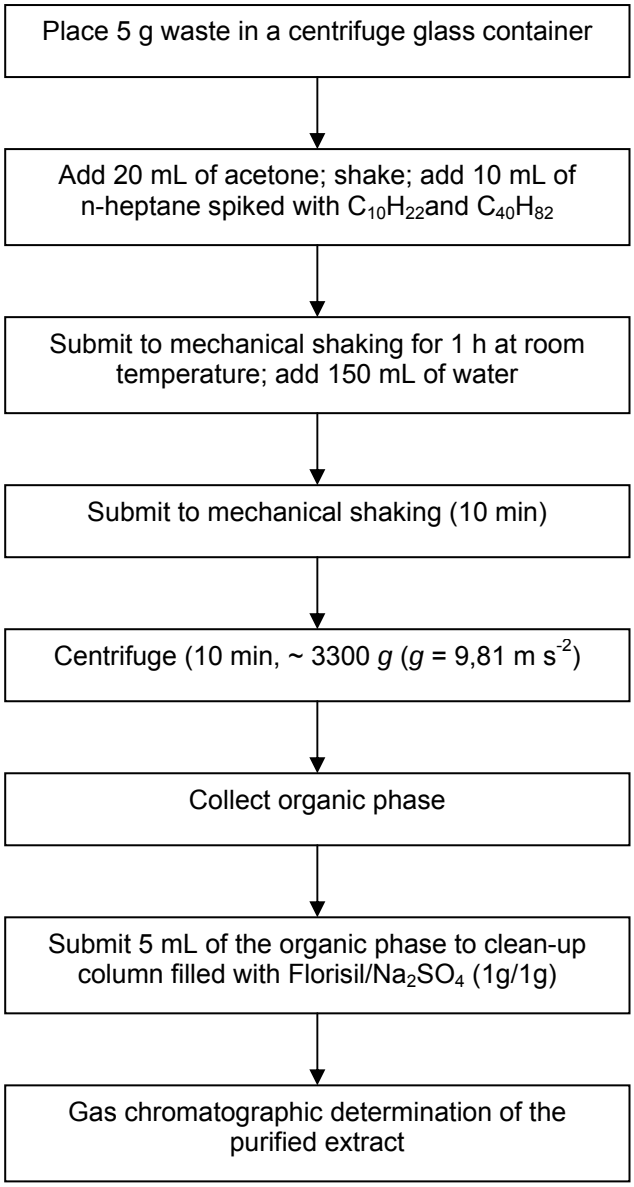


Fig. A3: GC-FID chromatogram of an extract of *Marine sediment*

ANNEX B: Analytical procedure (used for homogeneity and stability studies)



ANNEX C: Homogeneity study

Results of the homogeneity study on ERM-CC016.

Sample	Replicate determination							
No.	1	2	3	4	5	Mean	SD	RSD
	[mg kg^{-1}]	[mg kg^{-1}]	[mg kg^{-1}]	[mg kg^{-1}]	[mg kg^{-1}]	[mg kg^{-1}]	[mg kg^{-1}]	[%]
3	3234	2999	3159	3362	2991	3149	158	5,02
35	3001	3339	2934	2814	3073	3032	196	6,47
61	2941	2883	3295	2959	3244	3064	190	6,20
84	3336	3176	3055	3310	3028	3181	141	4,45
111	3076	3123	2963	2849	3180	3038	132	4,36
143	2848	3191	3070	3174	2966	3050	145	4,74
174	3152	2824	3523	3230	3480	3242	282	8,70
196	2997	2999	2948	3067	2878	2978	70	2,35
208	2992	2913	2827	3175	3288	3039	190	6,24
235	3119	3008	2958	2808	3333	3045	196	6,42
257	3456	3084	3251	3125	3186	3220	146	4,54
Mean						**3094**		

ANOVA	(5 g sample intake)					
Source of deviation	*Sum of squares (SS)*	*Degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*Critical F-value*
Between groups	385262,7	10	38526,3	1,253	0,286	2,054
Within groups	1352500,4	44	30738,6			
Total	1737763,1	54				

The uncertainty between bottles s_{bb} is calculated according to (1).

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

The relative uncertainty s_{bb_rel} is calculated according to (2)

$$s_{bb_rel} = \frac{s_{bb}}{\bar{x}} \qquad (2)$$

The contribution u_{bb} to the overall uncertainty is calculated according to (3)

$$u_{bb} = s_{bb_rel} \cdot w_{cert} \qquad (3)$$

$MS_{between}$	Mean squares between bottles
MS_{within}	Mean squares within bottles
n	Number of replicate measurements per selected bottle
$\bar{x}$	Mean value of homogeneity study
w_{cert}	Certified value of the mineral oil content

ANNEX D: Initial stability study

Results of the initial stability study on ERM®-CC016.

Storage temperature: +4°C

1 Month	Mineral oil [mg kg^{-1}]	3 Months	Mineral oil [mg kg^{-1}]	6 Months	Mineral oil [mg kg^{-1}]
248-1	3073	130-1	2350	059-1	2982
248-2	3000	130-2	2285	059-2	3021

Storage temperature: +20°C

1 Month	Mineral oil [mg kg^{-1}]	3 Months	Mineral oil [mg kg^{-1}]	6 Months	Mineral oil [mg kg^{-1}]
140-1	3078	020-1	1773	113-1	2886
140-2	3091	020-2	1824	113-2	2860

Storage temperature: +40°C

0,5 Month	Mineral oil [mg kg^{-1}]	1 Month	Mineral oil [mg kg^{-1}]	3 Months	Mineral oil [mg kg^{-1}]	6 Months	Mineral oil [mg kg^{-1}]
026-1	2609	231-1	2995	091-1	3141	183-1	2850
026-2	2638	231-2	3039	091-2	3086	183-2	2839

Storage temperature: +60°C

0,5 Month	Mineral oil [mg kg^{-1}]	1 Month	Mineral oil [mg kg^{-1}]	3 Months	Mineral oil [mg kg^{-1}]
206-1	2737	100-1	3063	157-1	3045
206-2	2784	100-2	3128	157-2	2987

Storage temperature: -20°C (Reference samples)

No.	Mineral oil [mg kg^{-1}]
043-1	3115
043-2	3194
162-1	3099
162-2	3125
261-1	3174
261-1	3203

ANNEX E: Method reporting sheet

Mineral oil hydrocarbons in soil/waste

Sample preparation

Extraction method:
Extraction time [h]:
Extraction temperature [°C]:
Extraction solvent:

Analyses carried out according to ISO 16703?

[ ] yes [ ] no

If "no", please describe the changes!

Clean-up carried out according to ISO 16703 using a Florisil- / Na_2SO_4 -column?

[ ] yes [ ] no

If "no", please describe the clean-up you have used!

GC-measurement conditions

GC-typ:

Detector: [x] FID *(prescribed according to ISO 16703!)*

Column (Length, phase, diameter, etc):
Carrier gas / flow:
Injection technique, e.g. on-column:
Injection volume [µl]:
Oven programme:

Integration: [x] Retention time range C_{10} to C_{40}
(prescribed according to ISO 16703!)

Diesel/Lubricating- calibration standard:

[ ] BAM-K010 [ ] other calibration standard

If another calibration standard than BAM-K010 used: Which?

Number of calibration points?

Hydrocarbon calibration levels:
Lowest calibration level [mg/ml]:
Highest calibration level [mg/ml]:

ANNEX F: Result reporting sheet

Mineral oil hydrocarbons in soil/waste

Note:

- Please perform 3 separate determinations per sample bottle
- Please mind the unit of the results
- Lot-No of the sample in indicated on the label

Results:

(please choose a sample intake of about 10 gram!)

soil/waste	Lot-No.		1	2	3
Sample A		**Sample intake (g)**			
		Hydrocarbon content (mg/kg)			
		Date			
Sample B		**Sample intake (g)**			
		Hydrocarbon content (mg/kg)			
		Date			

GC-control measurements:

Unknown solutions GC-1 and GC-2:
Retention time window compounds n-decane and n-tetracontane are already included.
(intended for direct GC-injection; a dilution is not necessary)

GC-control solution	Concentration (mg/ml)
GC-1	
GC-2	

Name of laboratory:
Operator:
Date:

ANNEX G: Results of certification study

Laboratory	Sample A			Sample B			GC control solutions	
	# 1	# 2	# 3	# 1	# 2	# 3	GC 1	GC 2
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg/mL	mg/mL
Lab 01	3734	3944	4051	4073	4230	4068	1,26	3,32
Lab 02	3110	3370	3420	3250	3710	3590	0,89	2,90
Lab 03	3066	3039	3056	2944	2928	3030	1,03	3,20
Lab 04	3283	3259	3269	3306	3203	3265	1,03	2,99
Lab 05	3756	3613	3434	3789	3806	3638	1,10	3,29
Lab 06	2980	3080	3130	3100	3170	3200	0,99	3,14
Lab 07	2992	2986	2924	3000	2922	2926	1,01	3,04
Lab 08	3231	3434	3402	3568	3542	3539	0,97	3,06
Lab 09	2662	2788	2690	2672	2894	2853	1,07	3,12
Lab 10	3525	3467	3516	3469	3598	3479	0,97	2,93
Lab 11	3190	3216	3150	3138	3160	3180	1,00	3,08
Lab 12	2690	2732	2724	2812	2812	2749	0,99	2,97
Lab 13	2588	2651	2549	2575	2543	2518	0,90	2,91
Lab 14	2810	2703	2677	2730	2884	2774	1,02	2,95