Institute for Reference Materials and Measurements

ERM European Reference Materials

CERTIFICATION REPORT

The Certification of the Mass Fractions of selected Polycyclic Aromatic Hydrocarbons (PAHs) in fine dust (PM_{10}-like matrix)

Certified Reference Material ERM®-CZ100

EUR 24578 EN – 2010

JRC EUROPEAN COMMISSION

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Joint Research Centre
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JRC 61262

EUR 24578 EN
ISBN 978-92-79-17528-2
ISSN 1018-5593
doi:10.2787/32299

Luxembourg: Publications Office of the European Union

Printed in Belgium

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The Certification of the Mass Fractions of selected Polycyclic Aromatic Hydrocarbons (PAHs) in fine dust (PM_{10}-like matrix)

Certified Reference Material ERM®-CZ100

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Summary

This report describes the preparation and certification of the new Reference Material (CRM) ERM-CZ100 PAHs in fine dust (PM_{10}-like).

Certification of the CRM included testing of the homogeneity and stability of the material as well as the characterisation using an intercomparison approach.

ERM-CZ100 was certified for its content of benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*j*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*c,d*]pyrene, dibenzo[*a,h*]anthracene and sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene.

The main purpose of the material is to assess method performance, i.e. for checking accuracy of analytical results in the field of air quality assurance. As any reference material, it can also be used for control charts or validation studies.

The certified values are listed below:

PAH	Mass Fraction	
	Certified value [1] [mg/kg]	Uncertainty [2] [mg/kg]
Benzo[*a*]anthracene	0.91	0.07
Benzo[*a*]pyrene	0.72	0.05
Benzo[*b*]fluoranthene	1.42	0.14
Benzo[*j*]fluoranthene	0.75	0.14
Benzo[*k*]fluoranthene	0.67	0.06
Dibenzo[*a,h*]anthracene	0.18	0.04
Indeno[1,2,3-*c,d*]pyrene	1.07	0.10
Sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene[3]	2.84	0.21

[1] The value is the unweighted mean of accepted sets of data, each set being obtained in a different laboratory and/or with a different method. The certified values are reported on the mass of the sample after conditioning the sample using conditions as described in EN12341 and are traceable to the SI.
[2] Expanded uncertainty with a coverage factor $k = 2$ according to the Guide to the Expression of Uncertainty in Measurement (GUM), corresponding to a level of confidence of about 95 %.
[3] The sum of the compounds was calculated as the sum of the individual certified values. The uncertainty was calculated as the combined expanded uncertainty of the uncertainties of the individual compounds.

The additional material information listed below:

PAH	Mass Fraction
	Value [1] [mg/kg]
Anthracene	0.28
Benzo[g,h,i]pyrene	1.76
Chrysene	1.61
Coronene	0.84
Fluoranthene	4.67
Phenanthrene	2.23
Pyrene	4.59

[1] The mean values for additional compounds came from the accepted data sets of the characterisation study. The values are reported on the mass of the sample after conditioning the sample using conditions as described in EN12341.

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Glossary

ANOVA	Analysis of variance
AQUILA	National Air Quality Reference Laboratories
ASE	Accelerated solvent extraction
BCR	Community Bureau of Reference
CRM	Certified Reference Material
Δ_m	Difference between mean measured value and the certified value
DG ENV	Directorate General for the Environment
DLS	Dynamic Light Scattering
EC	European Commission
ERM	European Reference Material
FLD	Fluorescence Detector
GC	Gas chromatography
HPLC	High Performance Liquid Chromatography
IDMS	Isotope Dilution Mass Spectrometry
IES	Institute for Environment and Sustainability
IRMM	Institute for Reference Materials and Measurements
JRC	Joint Research Centre
MS	Mass spectrometry
$MS_{between}$	Mean square between vials from an ANOVA
MS_{within}	Mean square within a vial from an ANOVA
n	Average number of replicates per vial
NIST	National Institute of Standards and Technology
PAH	Polycyclic Aromatic Hydrocarbon
PM_{10}	Particulate Matter of 10 µm and less aerodynamic diameter
PSA	Particle Size Analysis
Q_x	Cumulative distribution equal x vol. %
Q3	Percentage distribution of the particles
q3*	Volume distribution of the particles
RM Unit	Reference Materials Unit
RSD	Relative Standard Deviation
s	Standard deviation
SI	International System of Units
SIM	Selected Ion Monitoring
s_{bb}	Standard deviation between-units
SPE	Solid-phase extraction
t_{sl}	Shelf life
TSP	Total Suspended Particulate
u_{bb}	Standard uncertainty related to a possible between-bottle heterogeneity
u_{char}	Standard uncertainty of the characterisation
U_{CRM}	Expanded uncertainty of the certified value
u_{CRM}	Uncertainty of the certified value
u_{Δ}	Combined uncertainty of u_{mean} and u_{CRM}
U_{Δ}	Expanded uncertainty of u_{mean} and u_{CRM}
U_{Lab}	Expanded uncertainty given by laboratory within characterisation study
u_{lst}	Standard uncertainty of the long-term stability
u_{mean}	Measurement uncertainty
u_{rec}	Standard uncertainty related to possible between-bottle heterogeneity modelled as rectangular distribution
u_{sts}	Standard uncertainty of the short-term stability
u^*_{bb}	Maximum heterogeneity that could be hidden by method repeatability
V-KFT	Volumetric Karl-Fischer titration
$v_{MSwithin}$	Degrees of freedom of MS_{within}
x_i	Time point for the stability study

1. Introduction

The European Air Quality Directives, specifically 2008/50/EC [1] and 2004/107/EC [2], require the monitoring of arsenic, cadmium, nickel, lead and several polycyclic aromatic hydrocarbons (PAHs) in PM_{10} (particulate matter of 10 µm and less aerodynamic diameter) in ambient air. Laboratories in the Member States have to carry out measurements of the aforementioned analytes to verify compliance with target or limit values set in the Directives. Therefore, appropriate quality control tools need to be available to ensure the quality of measurement data. Certified Reference Materials (CRMs) and proficiency testing schemes are such essential tools for analytical quality control and checking of laboratory proficiency and data comparability. Currently, no suitable CRM is available with certified contents of arsenic, cadmium, nickel, lead and polycyclic aromatic hydrocarbons in a matrix that would sufficiently resemble airborne particulate matter (PM_{10}). Likewise, there is a lack of suitable quality control samples for the organisation of proficiency testing schemes as currently carried out by the JRC-IES (Joint Research Centre, Institute for Environment and Sustainability) for atmospheric pollutants.

Therefore, the feasibility of the production of Certified Reference Materials for arsenic, cadmium, nickel, lead and PAHs was evaluated at JRC IRMM (Joint Research Centre, Institute for Reference Materials and Measurements), funded by DG ENV (Directorate General for the Environment) [3]. The positive outcome of the feasibility study allowed for the production and certification of two CRMs, one for arsenic, cadmium, nickel, lead (ERM-CZ120) and one for selected PAHs (ERM-CZ100). The production and certification of the last is described in this report. This work was supported by funding of DG ENV.

2. Participants

2.1 Project management and evaluation

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
(accredited to ISO Guide 34 for production of certified reference materials, BELAC No 268-TEST)

2.2 Processing

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE
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2.3 Homogeneity and stability studies

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2.4 Characterisation study

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Wojewódzki Inspektorat Ochrony Środowiska we Wrocławiu delegatura w Jeleniej Górze, Jelenia Góra, PL
(accredited to ISO/IEC 17025, PCA, AB 075)

3. Processing of the material

3.1 Feasibility study

A feasibility study of the production of CRMs for arsenic, cadmium, nickel, lead and PAHs in a PM_{10}-like matrix were performed. Within the frame of the study, the following materials were evaluated in order to determine whether they are suitable for the production of the air quality CRMs: BCR-723 (a road dust certified for palladium, platinum and rhodium), BCR-605 (an urban road dust certified for trimethyllead), winter and summer filter dust (TSP (Total Suspended Particulate) collected from the ventilation system of IRMM buildings) and tunnel dust TSP collected from the walls of the road tunnel "Wisłostrada" in Warsaw.
The materials were tested for particle size distribution, content of the analytes, homogeneity and short-term stability. It was found that the summer filter dust, the winter filter dust and the tunnel dust could be used for production of CRMs [3].
However, the tunnel dust material was selected for the production and certification of the elements and PAHs because the amount of this material (~12 kg) was sufficient for this purpose while for the filter dust additional material collection would have to be performed which would have taken at least another year.

3.2 Processing of the tunnel dust material

The material originates from the road tunnel “Wisłostrada” in Warsaw, Poland. The tunnel is approximately 900 m in length and is a major traffic route through the city. The dust was collected mainly from the tunnel walls and partly from the tunnel sidewalks inaccessible to people. The material was separated from the coarse particles by sieving (0.5 mm sieve followed by 0.250 mm sieve) and then ground using a jet mill to finally obtain a very fine dust with 10 vol.% of particles below 1.75 µm, 16 vol.% of particles below 2.49 µm, 50 vol.% of particles below 7.59 µm, 84 vol.% of particles below 15.01 µm and 90 vol.% of particles below 20 µm (see Table 1) [4]. The resulting material was stored at 4 °C to avoid losses of volatile analytes.

Table 1: Particle size distribution of the tunnel dust

Tunnel dust	Upper particle size ± expanded uncertainty[a] [µm]					
	Q_{10}[b]	Q_{16}[b]	Q_{50}[b]	Q_{84}[b]	Q_{90}[b]	Q_{100}[b]
	1.75 ± 0.08	2.49 ± 0.10	7.59 ± 0.33	15.01 ± 0.72	17.57 ± 0.84	73

[a]: as measured using DLS (Dynamic Light Scattering) with a coverage factor k = 2 corresponding to a level of confidence of about 95 %
[b]: $Q_{10,\ 16,\ 50,\ 84,\ 90,\ \text{and}\ 100}$ – cumulative distribution equals 10 vol.%, 16 vol.%, 50 vol.%, 84 vol.%, 90 vol.% and 100 vol.%, respectively

Airborne particles have irregular shapes, and their aerodynamic behaviour is expressed in terms of the diameter of an idealised spherical particle known as aerodynamic diameter. Particles are sampled and described on the basis of their aerodynamic diameter, which is usually simply referred to as particle size. However, particles having the same aerodynamic diameter may have different dimensions and shapes. For practical purpose, particle size distribution were measured by DLS in a dispersion and are only indicative of the aerodynamic diameter of the particles.

Particle size distribution was measured in the PSA (Particle size analysis) laboratory of the RM Unit, IRMM by means of a laser light diffraction technique. The measurements were performed using a SYMPATEC Helos (Clausthal-Zellerfeld, Germany) equipped with a 50 mL cuvette. The measurement time was 10 s and the stirrer rate was 1200 revolutions per minute. The sample was dispersed in 2-propanol.

The results are presented in Figure 1.

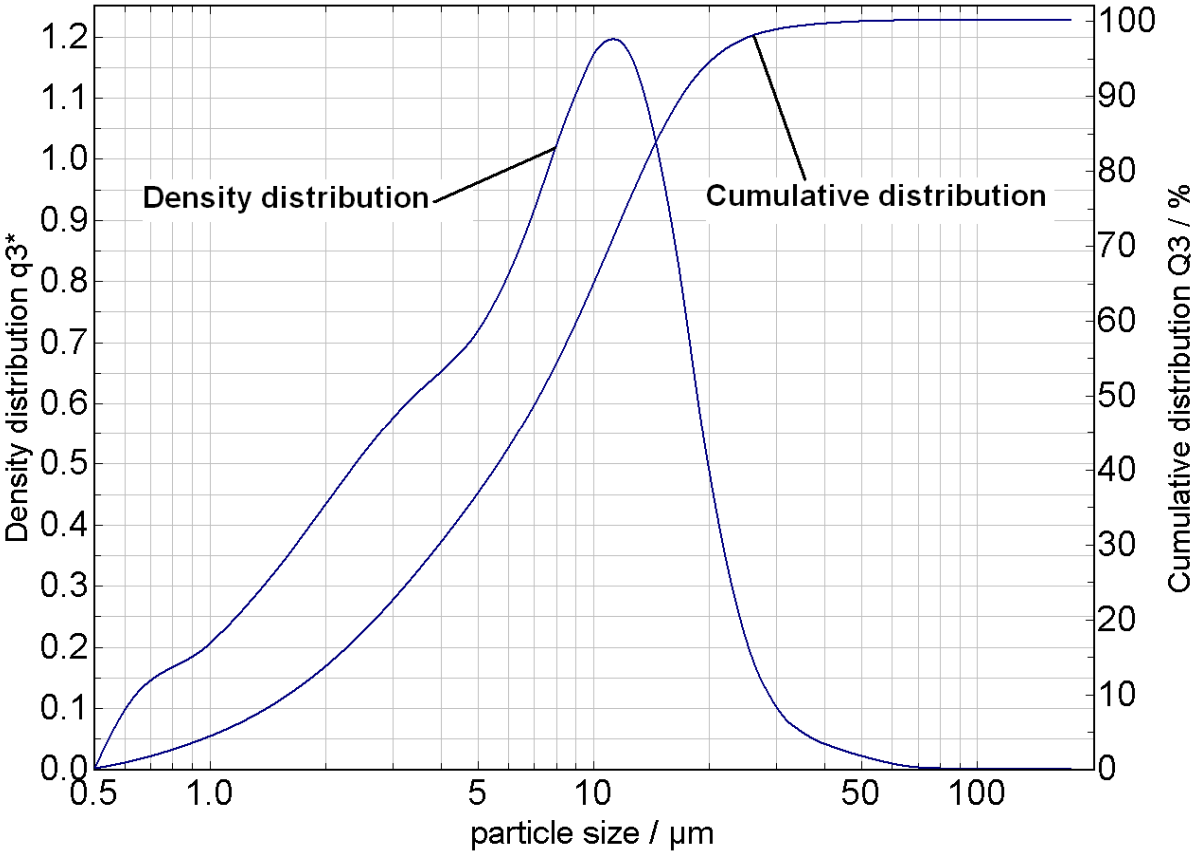


Figure 1: Particle size distribution (in vol. %)

The density curve gives the volume distribution (q3*) of the particles as a function of the equivalent sphere diameter. The cumulative curve shows percentage distribution (Q3) as a function of the particles diameters.

To take the micrographs a portion of dust was deposited on a stub covered with an adhesive carbon tape. Then it was coated with gold for 2 minutes at 20 mA (Emitech K550X Sputter Coater), corresponding to a nominal gold layer thickness of 15 nm. The micrographs were obtained using a Zeiss microscope Stemi 2000-C (PSA laboratory of the RM Unit, IRMM) and an electron microscope: dual-beam FIB-SEM Quanta 200/3D (Engineering Materials Laboratory of the RM Unit, IRMM).

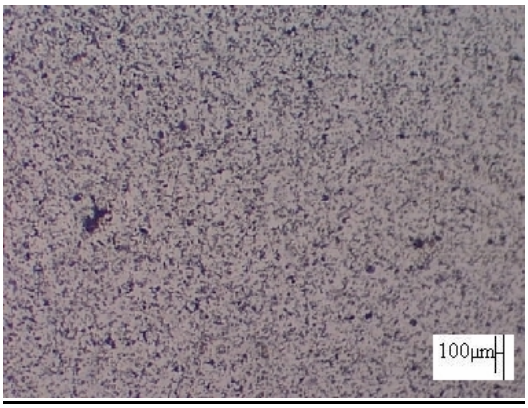


Figure 2: Micrographs obtained using a Zeiss microscope Stemi 2000-C

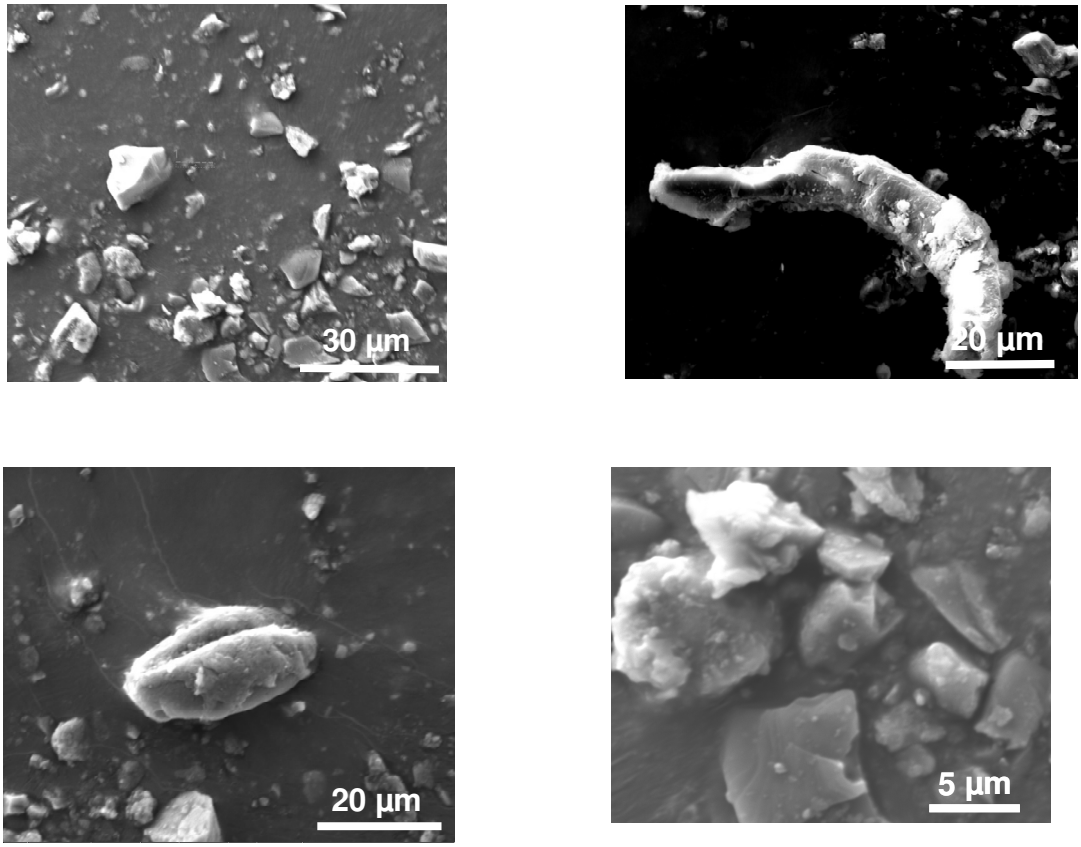


Figure 3: Micrographs with different magnifications obtained using an electron microscope dual-beam FIB-SEM Quanta 200/3D

A typical material morphology is shown in Figure 2. Micrographs were obtained using a Zeiss microscope Stemi 2000-C. In Figure 3 (larger magnifications), the images show different structures found in the material that are not representative of the bulk material. As shown, the material consists of a large variety of particles (spheres, cubes, fibres, irregular shapes).

The water content determined in the final product using volumetric Karl Fischer titration (V-KFT, Metrohm Ltd, Herisau, CH) was 2.68 % (m/m) ± 0.30 % (m/m) (average of three measurements on each of ten vials, expanded uncertainty with a coverage factor of $k = 2$).

Material filling

The material was filled into 5 mL amber glass vials, closed with a rubber stopper (coated with PTFE) and an aluminium cap under argon atmosphere. Each vial contains about 0.5 g of the material.

4. Homogeneity study

4.1 Between-bottle homogeneity

The between-bottle homogeneity was evaluated to ensure that the certified values of the CRM are valid for all vials of the material, within the stated uncertainty.

For the homogeneity test, eighteen vials of the material were selected using a random stratified sampling scheme. The number of selected vials corresponds to approximately the cubic root of the total number of the produced units.

From each vials three independent replicates were prepared. The vials were shaken for about 10 min before opening. However, during the validation of the method, it was concluded that 2 min of shaking of the sample before opening is enough for sample rehomogenisation. Therefore, for other studies (the short-term stability study, the long-term stability study and the characterisation study) samples were shaken 2 min before opening. The same time is recommended in the instructions for use (section 9.3). About 100 - 150 mg sample was extracted with dichloromethane using an ASE (Accelerated Solvent Extraction) system. The obtained extracts were cleaned using aminopropylsilane SPE (Solid-phase Extraction) cartridges. The measurements with respect to the content of benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*j*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*c,d*]pyrene and dibenzo[*a,h*]anthracene were performed by means of a GC-IDMS (Gas Chromatography Isotope Dilution Mass Spectrometry) in the SIM (Selected Ion Monitoring) mode and with a DB-17HT column.

The results (mass fractions) are reported based on the mass of the sample prepared as taken from the vial.

The measurements were carried out in a randomised sequence to be able to separate a potential analytical drift from a trend in the filling sequence.

On the obtained data, Grubbs-tests were performed to detect potentially outlying individual results and outlying vial averages.

Some outlying individual results were found for benzo[*b*]fluoranthene and indeno[1,2,3-*c,d*]pyrene, and one outlying vial average was found for benzo[*a*]pyrene (see Annex A, benzo[*a*]pyrene, and vial no. 293). Since no technical reasons were found for the outlying results all data were retained for statistical analysis.

Consequently, regression analyses were performed to evaluate potential trends in the analytical sequence and trends in the filling sequence. For both the analytical sequence and the filling sequence, no trends were found.

The obtained data were first tested as to whether they follow a normal, or at least unimodal distribution. This was done by visual inspection of normal probability plots and histograms (if the data do not follow at least a unimodal distribution, the calculation of standard deviations would be inappropriate). All individual results were normally and unimodally distributed.

The results were then evaluated by a one-way analysis of variance (ANOVA). From the results of the ANOVA calculation, the following figures were determined:

Between-bottle standard deviation (s_{bb}) as given by:

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}}\,, \tag{1}$$

where:

$MS_{between}$: mean squares between-bottle from an ANOVA
MS_{within}: mean squares within-bottle from an ANOVA
n: average number of replicates per vial

The maximum heterogeneity that can be hidden by the method repeatability (which is used as the minimum uncertainty contribution from homogeneity) defined by:

$$u_{bb}^{*} = \sqrt{\frac{MS_{within}}{n}}\sqrt[4]{\frac{2}{v_{MSwithin}}}\,, \tag{2}$$

where:

$v_{MSwithin}$: degrees of freedom of MS_{within}

The larger value of s_{bb} or u^*_{bb} was used as uncertainty contribution from the homogeneity, u_{bb}. However, a different approach was adopted for benzo[*a*]pyrene for which one outlying vial average was detected. In this case, between-bottle heterogeneity was modelled as a rectangular distribution limited by the widest outlying vial average, and the rectangular standard uncertainty of homogeneity was estimated as given by:

$$u_{rec} = \frac{\left|\text{widest outlying vial avarage} - \overline{x}\right|}{\sqrt{3}}, \quad (3)$$

where:

$\overline{x}$: average of all results of the homogeneity study.

The results of the measurements are shown in Annex A (homogeneity study).

The results of evaluation are summarised in Table 2.

Table 2: Results of the homogeneity study for content of PAHs in ERM-CZ100 material

PAH	s_{bb}	u^*_{bb}	u_{rec}	u_{bb}
	[%]	[%]	[%]	[%]
Benzo[*a*]anthracene	0.6	0.7	-	0.7
Benzo[*a*]pyrene	0.5	0.5	1.6	1.6
Benzo[*b*]fluoranthene	1.3	0.5	-	1.3
Benzo[*j*]fluoranthene	n.c.	1.0	-	1.0
Benzo[*k*]fluoranthene	1.0	0.7	-	1.0
Dibenzo[*a,h*]anthracene	1.4	0.9	-	1.4
Indeno[1,2,3-*c,d*]pyrene	0.9	0.6	-	0.9

n.c. = cannot be calculated as $MS_{between} < MS_{within}$

The potential between-unit variation is generally below 2 %. This material is therefore sufficiently homogeneous to be suitable as a reference material.

4.2 Minimum sample intake

The minimum sample intake is the minimum amount of sample that is representative for the whole unit. Samples equal or above the minimum sample intake guarantee the certified value within its stated uncertainty.

To estimate of the minimum sample intake a series of measurements with decreasing amount of sample for one randomly selected vial were performed. The following sample intakes were tested: 50 mg, 40 mg and 30 mg. From each sample intake 6 samples were prepared. The samples were prepared in the same way as in case of samples of the homogeneity study (see section 4.1).

The results (mass fractions) are reported based on the mass of the sample prepared as taken from the vial.

The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend related to the sample intake.

The minimum sample intake was established by comparison of variances obtained for 50 mg, 40 mg and 30 mg sample intakes with the variance obtained for results of the

homogeneity study samples (100 - 150 mg sample intake). It was done using an F-test for equality of two samples for variances with degrees of freedom of 5 and a confidence level of 95 %.

The minimum sample intakes are shown in the Table 3.

The individual values obtained during measurements related to the establishment of the minimum sample intake are shown in Annex B. The individual values obtained for sample intake 150 mg and 100 mg in the homogeneity study are shown in the Annex A.

Table 3: Minimum sample intake

PAH	Minimum sample intake [mg]
Benzo[*a*]anthracene	50
Benzo[*a*]pyrene	50
Benzo[*b*]fluoranthene	50
Benzo[*j*]fluoranthene	40
Benzo[*k*]fluoranthene	50
Dibenzo[*a,h*]anthracene	50
Indeno[1,2,3-*c,d*]pyrene	50
Sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene	50*

*The minimum sample intake of a 50 mg is also valid for the sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene because the sum was calculated as the sum of the individual values obtained for these compounds.

As shown in Table 3 a minimum sample intake of 50 mg was established for all PAHs. However, in case of benzo[*j*]fluoranthene the material can be analysed with 40 mg sample intake as well.

5. Stability study

Stability testing is necessary to establish conditions for storage (long-term stability) as well as conditions for dispatch to the customers (short-term stability). The stability studies were carried out using an isochronous design [5]. In that approach, samples are stored for a certain time at different temperature conditions. Afterwards, the samples are moved to conditions where further degradation can be assumed to be negligible ("reference conditions"). At the end of the isochronous storage the samples are analysed simultaneously under repeatability conditions. Analysis of the material (after various exposure times and temperatures) under repeatability conditions greatly improves the sensitivity of the stability tests. Time, temperature and light (UV-radiation) were regarded as the most relevant influences on stability of the material. The influence of UV-radiation was minimised by the choice of a brown glass vials, which eliminates most of the incoming light. In addition, materials are stored and dispatched in the dark, thus practically eliminating the possibility of degradation by UV-radiation. Therefore, only the influences of time and temperature needed to be investigated.

5.1 Short-term stability study

The short-term stability samples were stored for 0, 1, 2 and 4 weeks at 4 °C and 18 °C. The reference temperature was -20 °C. Two samples per storage time were selected using a random stratified sampling scheme. From each vial, three samples were prepared in the same way as in the case of samples in the homogeneity study (see section 4.1).
The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend over storage time.

The results (mass fractions) are reported based on the mass of the sample prepared as taken from the vial.

The results were screened for outlying values using a Grubbs-test. No outliers were found.

The data points obtained were plotted against storage time at the test temperature and the regression line was calculated. The slope of the regression line was then tested for statistical significance. The results of the short-term stability study are shown in Table 4.

The short-term stability graphs are shown in the Annex C.

Table 4: Results of the short-them stability study for content of PAHs in the ERM-CZ100, Fine Dust (PM_{10}-like). Reference temperature -20 °C

PAH	Slope significant on 95 % confidence level	u_{sts} [%/week]	Number of individual outlying results
Test temperature: 4 °C			
Benzo[*a*]anthracene	no	0.3	none
Benzo[*a*]pyrene	no	0.3	none
Benzo[*b*]fluoranthene	no	0.3	none
Benzo[*j*]fluoranthene	no	0.3	none
Benzo[*k*]fluoranthene	no	0.3	none
Dibenzo[*a,h*]anthracene	no	0.3	none
Indeno[1,2,3-*c,d*]pyrene	no	0.4	none
Sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene	no	0.3	none
Test temperature: 18 °C			
Benzo[*a*]anthracene	no	0.3	none
Benzo[*a*]pyrene	no	0.3	none
Benzo[*b*]fluoranthene	no	0.3	none
Benzo[*j*]fluoranthene	no	0.3	none
Benzo[*k*]fluoranthene	no	0.3	none
Dibenzo[*a,h*]anthracene	no	0.3	none
Indeno[1,2,3-*c,d*]pyrene	no	0.3	none
Sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene	no	0.3	none

The calculated uncertainties (u_{sts}) for the short-term stability study were between 0.3 % and 0.4 % for all compounds. Therefore the potential degradation due to dispatch are negligible. The uncertainty contribution from the short-term stability is not considered in the estimation of the total uncertainty of the material.

It was concluded that the material is stable at 4 ºC and 18 ºC up to 4 weeks. The samples can be safely dispatched under conditions where the temperatures do not exceed 18 ºC for up to 4 weeks, i.e. using cooling elements.

5.2 Long-term stability study

The results of the two long-term stability studies at + 4 °C (1st scheme lasting 12 months and 2nd scheme lasting 24 months) were combined and evaluated together to obtain more confidence about the assessment of the stability. The results are summarised in Table 5 (graphical depictions of the data can be found in Annex D).

Two samples per each storage time were selected using a random stratified sampling scheme. From each vial, three samples were prepared in the same way as in the case of samples in the homogeneity study (see section 4.1).

The results (mass fractions) are reported based on the mass of the sample prepared as taken from the vial.

The measurements were performed under repeatability conditions, and in a randomised manner to be able to separate a potential analytical drift from a trend over storage time.

The results were screened for outlying values using a Grubbs-test. Two outlying individual results were found for dibenzo[*a,h*]anthracene.

The data points obtained were plotted against storage time at the test temperature and the regression line was calculated. The slope of the regression line was then tested for statistical significance. No significant slope was detected.

The uncertainty of stability u_{lts} of the materials was calculated as uncertainty of the slope of the regression line multiplied with the chosen shelf life:

$$u_{lts} = \frac{s}{\sqrt{\sum \left(x_i - \bar{x}\right)^2}} \cdot t_{sl} \qquad (4)$$

where:

s: standard deviation of all results of the stability study
x_i: time point for each replicate
$\bar{x}$: average of all time points
t_{sl}: proposed shelf life (48 months at 4 ºC in this case)

The long-term stability study results are shown in Table 5.

Table 5: Results of the evaluation of the 12 and 24 months long-term stability studies for ERM-CZ100 at +4 °C. The given u_{lts} is the projected estimate based on a 48 months shelf life

PAH	Slope significant on 95 % confidence level	u_{lts} [%/48 months]	Number of individual outlying results
Benzo[*a*]anthracene	no	2.4	none
Benzo[*a*]pyrene	no	2.4	none
Benzo[*b*]fluoranthene	no	2.4	none
Benzo[*j*]fluoranthene	no	2.9	none
Benzo[*k*]fluoranthene	no	2.7	none
Dibenzo[*a,h*]anthracene	no	2.7	1[a], 1[b]
Indeno[1,2,3-*c,d*]pyrene	no	1.9	none

[a]: outlier on a 95 % confidence level
[b]: outlier on a 99 % confidence level

Graphical representations of the long-term stability results are given in Annex D. The results show that the material is stable at 4 °C. Uncertainties of stability during storage range from 1.9 to 2.9 % (based on a projected 48 months shelf-life). These uncertainties were taken up to the final uncertainties of the certified values. The shelf life will be revised, based on the results of the long-term stability study for 48 months isochronous storage and further stability monitoring.

6. Material characterisation

6.1 Approach

The material characterisation was based on a laboratory intercomparison approach, i.e. the content of selected PAHs in the material was determined in different laboratories that applied different measurement procedures to avoid method dependant bias.

Participants for the characterisation study were selected based on criteria that comprised both technical and quality management aspects. Fulfilment of the quality management requirements ensured the technical competence of the laboratory. Each participant was required to operate a quality system and to deliver documented evidence of its laboratory proficiency in the field of PAHs measurements in relevant matrices. Having an accreditation was not mandatory. However, when applicable the accreditation scope is stated in the list of participants.

The characterisation exercise started in August 2009 and finished in March 2010. Eighteen laboratories participated in this study.

The characterisation samples were selected using a random stratified sampling scheme and covered the whole batch.

Each laboratory received two vials of ERM-CZ100 and was requested to provide 6 independent results, 3 per vial. In case laboratories offered two different methods for the determination of PAHs, they received 4 vials (2 vials for each method). The sample weighing had to be performed using conditions (i.e. temperature humidity and time) that are specified in the standard EN 12341 [6]. It means that before analysis, the sample had to be opened and kept for at least 48 h in the air-conditioned weighing room with a temperature of 20 ± 1 °C and a relative humidity of 50 ± 5 % to reach equilibrium under weighing room conditions.

The sample preparations and measurements had to be spread over two days.

As a control sample, the participants received a sample of SRM NIST 2585 "Organic Contaminants in House Dust" to perform a single analysis. All compounds determined in the frame of the characterisation study were certified in this material. The certified values and the expanded uncertainties for selected compounds were as follows:
1.160 mg/kg ± 0.054 mg/kg for benzo[*a*]anthracene,
2.700 mg/kg ± 0.090 mg/kg for benzo[*b*]fluoranthene,
1.320 mg/kg ± 0.110 mg/kg for benzo[*k*]fluoranthene,
1.330 mg/kg ± 0.110 mg/kg for benzo[*j*]fluoranthene,
1.140 mg/kg ± 0.010 mg/kg for benzo[*a*]pyrene,
2.080 mg/kg ± 0.100 mg/kg for indeno[1,2,3-*c,d*]pyrene,
0.301 mg/kg ± 0.050 mg/kg for dibenzo[*a,h*]anthracene.
The results for this sample were used only to support the evaluation of the characterisation results (to confirm outliers, see Section 6.3), and are therefore not reported here.

6.2 Methods used

The methods that can be used in the characterisation study are defined in the Standard Method EN 15549 [7]. In the standard, several methods of PAHs extraction (extraction under reflux, soxhlet extraction, microwave extraction, ASE, ultrasonic extraction) and two methods of PAHs quantification (GC/MS and HPLC/FLD (High Performance Liquid Chromatography with Fluorescence Detector)) are pointed out.

All methods used during the characterisation study are summarised in Annex E. The lab-method code consists of a number assigned to each laboratory and abbreviation of the measurement method used (e.g. L01(GC/MS) or L01(HPLC/FLD)).

6.3 Evaluation of results

The characterisation campaign resulted in 6 to 9 datasets per compound. All individual results of the participants, grouped per compound are shown in tabular and/or graphical form in Annex F.

The obtained data were first checked for compliance with the requested analysis protocol and for their validity based on technical reasons. The following criteria were considered during the evaluation:

- compliance with the analysis protocol: weighing conditions, sample preparations and measurements performed on two days, analysis order;
- absence of 'less than' values,
- the sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene had to be calculated based on the individual values of the compounds;
- method performance, i.e. delivery of incorrect results for more than half of the analysed compounds within one quantification method clearly indicates that the method is not under control. This was verified with the QC sample. A result is considered incorrect when the combined standard uncertainty of the measurement of the QC sample and of the certified value does not cover the difference between the certified value and the measurement [8].

Based on the above some datasets were rejected as not technically valid (see Table 6).

Table 6: Datasets that shown non-compliances with the analysis protocol and technical specifications, and action taken

Lab-method code	PAH	Description of problem	Action taken
L01(GC/MS)	All compounds	Weighing was not performed according to the standard EN12341	Results rejected as not technically valid
L02(GC/MS)	All compounds	Laboratory was determining benzo[*b*]fluoranthene and benzo[*k*]fluoranthene using a DB-5 column. This column is not suitable for the separation of these compounds. Incorrect results for more than half of the analysed compounds in the QC sample.	Results rejected as not technically valid
L04(HPLC/FLD)	All compounds	Weighing was not performed according to the standard EN12341	Results rejected as not technically valid
L05(GC/MS)	All compounds	Weighing was not performed according to the standard EN12341	Results rejected as not technically valid
L06(HPLC/FLD)	All compounds	Incorrect results for more than half of the analysed compounds in the QC sample	Results rejected as not technically valid
L07(GC/MS)	All compounds	Due to technical problems lab did not deliver the results	-
L10(GC/MS)	All compounds	Incorrect results for more than half of the analysed compounds in the QC sample	Results rejected as not technically valid
L11(GC/MS)	Sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene.	The sum was not calculated based on the individual values of the compounds	Results rejected as not technically valid
L14(GC/MS)	All compounds	Weighing was not performed according to the standard EN12341	Results rejected as not technically valid
L16(HPLC/FLD)	All compounds	The sample preparation was not performed in agreement with the analysis protocol (within one day instead of two days)	Results rejected as not technically valid

The datasets accepted on technical grounds were tested for outlying laboratories using Dixon, Grubbs and Nalimov t-test. Them mean benzo[*j*]fluoranthene value from Laboratory 17 was identified as an outlier. No technical reason was found for excluding this mean and, considering the associated measurement uncertainty reported by the concerned laboratory, the mean value is not significantly different from the certified value. Therefore, the result was retained for the calculation of the mean and uncertainty of characterization value (u_{char}).

The certified value was calculated as the mean of means of the accepted datasets. The contribution of the material characterisation to the uncertainty of the certified value u_{char} was estimated as the standard error of the mean of means, and was calculated as the relative standard deviation divided by the square root of the number of accepted datasets. The resulting data are summarised in Table 7.

The results of characterisation study are showed in the Annex F.

Table 7: Summary of the characterisation study of ERM-CZ100

PAH	Number of independent, valid datasets	Mean of laboratory means [mg/kg]	u_{char} [%]
Benzo[*a*]anthracene	9	0.91	2.4
Benzo[*a*]pyrene	9	0.72	1.2
Benzo[*b*]fluoranthene	8	1.42	4.1
Benzo[*j*]fluoranthene	6	0.75	8.8
Benzo[*k*]fluoranthene	8	0.67	2.5
Dibenzo[*a,h*]anthracene	7	0.18	10.5
Indeno[1,2,3-*c,d*]pyrene	9	1.07	3.7

7. Assigned values

7.1 Certified values and their uncertainties

The unweighted mean of the means of the accepted datasets as shown in Table 8 was assigned as a certified value for the selected compounds.

The certified uncertainty consists of uncertainties related to characterisation, $u_{char,\ rel}$ (see Section 6.3), between-bottle heterogeneity, $u_{bb,\ rel}$ (see Section 4.1) and degradation during long-term storage, $u_{lts,\ rel}$ (see Section 5.2). These different contributions were combined to estimate the expanded, relative uncertainty of the certified value (U_{CRM}) as given by:

$$U_{CRM} = k \cdot \sqrt{u^2_{char,\,rel} + u^2_{bb,\,rel} + u^2_{lts,\,rel}} \qquad (5)$$

where:

k: coverage factor equalling 2, representing a level of confidence of about 95 %.

The certified values and their uncertainties are summarised in Table 8.

Table 8: Certified values and their uncertainties for ERM-CZ100

PAH	Certified value [mg/kg]	U_{CRM} [mg/kg]	$u_{char,\ rel}$ [%]	$u_{bb,\ rel}$ [%]	$u_{lts,\ rel}$ [%]	$U_{CRM,\ rel}$ [%]
Benzo[*a*]anthracene	0.91	0.07	2.4	0.7	2.4	6.9
Benzo[*a*]pyrene	0.72	0.05	1.2	1.6	2.4	6.3
Benzo[*b*]fluoranthene	1.42	0.14	4.1	1.3	2.4	9.7
Benzo[*j*]fluoranthene	0.75	0.14	8.8	1.0	2.9	18.6
Benzo[*k*]fluoranthene	0.67	0.06	2.5	1.0	2.7	7.6
Dibenzo[*a,h*]anthracene	0.18	0.04	10.5	1.4	2.7	21.8
Indeno[1,2,3-*c,d*]pyrene	1.07	0.10	3.7	0.9	1.9	8.6
Sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene	2.84*	0.21**	-	-	-	7.4

* The sum of the compounds was calculated as the sum of the individual certified values. The uncertainty was calculated as the combined expanded uncertainty of the uncertainties of the individual compounds.

** The uncertainty was calculated as the combined expanded uncertainty of the uncertainties of the individual compounds.

7.2 Additional material information

Additional information is available for some others PAHs, which were not certified. The data is in the Table 9. The mass fractions of the listed PAHs represent the mean value of the results provided by laboratories in the characterisation study. In the table, the mean value of

the mass fraction, the standard deviation and the number of data sets for the respective PAHs are given.

Table 9: Additional material information

PAH	Mean of laboratory means [mg/kg]	*s* [mg/kg]	Number of data sets
Anthracene	0.28	0.07	3
Benzo[*g*,*h*,*i*]pyrene	1.76	0.31	3
Chrysene	1.61	0.29	3
Coronene	0.84	0.02	1
Fluoranthene	4.67	0.58	3
Phenanthrene	2.23	0.33	4
Pyrene	4.59	0.81	3

8. Metrological traceability and commutability

8.1 Metrological traceability

Traceability of the certified values to the SI is ensured through the set-up of the characterisation. The participating laboratories used a number of different methods for the sample preparation and two methods for the final determination, thus eliminating any possibility of method dependent results (see Annex E). In addition, different calibrants were used, including commercial standard solutions and CRMs. Most of the laboratories also used matrix CRMs for quality control (see Annex E).
Traceability of the certified value of the sum parameter to the SI is ensured through the set-up of the characterisation as the sum was calculated based on the individual results and the individual uncertainties of relevant for each compound.

8.2 Commutability

Commutable CRMs should exhibit a similar analytical behaviour for given methods as a real laboratory sample. The CRM was prepared for laboratories doing the air quality measurements. Most of laboratories participating in the characterisation belong to National Air Quality Reference Laboratories (AQUILA), which all use the preparation methods and the determination methods according to the standards EN 12341 [6] and EN 15549 [7]. However, few laboratories prepared the samples using in-house developed methods of sample preparation. The good agreement between the results obtained according to different methods of sample preparation indicates commutability of the material.
Commutability of the material can also be confirmed by the results of the feasibility study performed before production and certification of the material. The study was performed in cooperation with voluntary laboratories of the AQUILA group as well. The evaluation of the results has shown that the tunnel dust was suitable as a PM_{10} material in terms of the analytes content and material handling. In addition, in the most cases the results of the material determination with the respect to the content of PAHs are in agreement among laboratories [3].

9. Instructions for use

9.1 Storage conditions

The material shall be stored at 4 °C ± 3 °C in the darkness. However, the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened samples.

9.2 Safety and protection for the environment

The usual laboratory safety measures apply. As the material consists of fine particles, appropriate protection against inhalation is recommended.

9.3 Use of the material

The vials shall be shaken at least 2 min before opening to ensure the material re-homogenisation. The sample weighing shall be performed using conditions (i.e. temperature humidity and time) that are specified in the standard EN 12341 [6]. It means that before analysis, the sample has to be opened and kept for at least 48 h in the air-conditioned weighing room with a temperature of 20 °C ± 1 °C and a relative humidity of 50 % ± 5 % to reach equilibrium under weighing room conditions.

9.4 Minimum sample intake

The minimum sample intake representative for all PAHs is 50 mg.

9.5 Use of the certified value

The main purpose of the material is to assess method performance, i.e. for checking accuracy of analytical results. As any reference material, it can also be used for control charts or validation studies.

For assessing the method performance, the measured values of the CRMs are compared with the certified values following a procedure described by Linsinger [8]. The procedure is described here in brief:

- Calculate the absolute difference between mean measured value and the certified value (Δ_m).
- Combine measurement uncertainty (u_{mean}) with the uncertainty of the certified value (u_{CRM}): $u_\Delta = \sqrt{u_{mean}^2 + u_{CRM}^2}$
- Calculate the expanded uncertainty (U_Δ) from the combined uncertainty (u_Δ) using a coverage factor of two ($k = 2$), corresponding to a confidence interval of approximately 95 %
- If $\Delta_m \leq U_\Delta$ then there is no significant difference between the measurement result and the certified value, at a confidence level of about 95 %.

Use as a calibrant

It is not recommended to use matrix materials as calibrants. If used nevertheless, the uncertainty of the certified value shall be taken into account in the estimation of the measurement uncertainty.

References

[1] Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, http://eur-lex.europa.eu;
[2] Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, http://eur-lex.europa.eu;
[3] Perez Przyk, E., Held, A., Charoud-Got, J., 2008, Development of particulate matter certified reference materials (PM_{10} CRMs). Final Report. Administrative Arrangement no. 070402/2006/438490/MAR/C3 Feasibility study for the production of certified reference materials for the selected PAH compounds and heavy metals in the PM_{10} matrix EUR 23244 EN, ISBN 978-92-79-08347-1, Luxembourg: Office for Official Publications of the European Communities;
[4] Preparation of ERM-CZ100 PAHs in fine dust (PM_{10}-like) and ERM-CZ12, trace elements in fine dust (PM_{10}-like), Final report, RM-10-002, internal report, private communication;
[5] Lamberty A., H. Schimmel and J. Pauwels, 1998, The study of the stability of reference materials by isochronous measurements, *Fresenius J Anal Chem*, 360, 359 - 361.
[6] EN 12341:1998, Air quality - Determination of the PM_{10} fraction of suspended particulate matter – Reference method and field test procedure to demonstrate reference equivalence of measurement methods;
[7] EN 15549:2008, Air quality - Standard method for the measurement of the concentration of benzo[a]pyrene in ambient air;
[8] T. Linsinger, 2010, ERM Application Note 1, www.erm-crm.org;

Acknowledgments

The financial support by DG Environment (Administrative Arrangement no. 070307/2007/478944/MAR/C3 "Production of certified reference materials for the selected PAH compounds and heavy metals in the PM_{10} matrix") is gratefully acknowledged.

The authors would like to thank K. Teipel, M-F. Tumba-Tshilumba, J. Charoud-Got, H. Emteborg, G. Kerckhove and B. Sejeroe-Olsen from the RM Unit, IRMM for their support and help.

The authors would like also to thank I. Zegers and J. F. Huertas-Perez (IRMM, BE) for internal review of this report as well as P. Gowik (Federal Office of Consumer Protection and Food Safety, DE), P. Finglas (Institute of Food Research, GB) and J. de Boer (Institute for Environmental Studies, VU University Amsterdam, NL) as members of the Certification Advisory Panel for reviewing the certification documents and for their constructive comments.

Annexes

Annex A: Results of the homogeneity study, ERM-CZ100
Annex B: Minimum sample intake, ERM-CZ100
Annex C: Results of the short-term stability study, ERM-CZ100
Annex D: Results of the long-term stability study, ERM-CZ100
Annex E: Characterisation study – laboratories and methods, ERM-CZ100
Annex F: Characterisation study – results, ERM-CZ100
Annex G: Additional material information, ERM-CZ100

Annex A: Results of the homogeneity study, ERM-CZ100

benzo[*a*]anthracene

Vial number	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]
70	41	0.879	46	0.859	51	0.897
184	26	0.858	31	0.867	36	0.875
293	44	0.898	43	0.851	48	0.894
416	53	0.904	25	0.885	30	0.833
515	35	0.854	40	0.890	45	0.853
584	49	0.871	50	0.878	54	0.915
709	42	0.884	47	0.876	52	0.895
846	12	0.896	7	0.889	2	0.882
918	27	0.847	32	0.868	37	0.881
1070	13	0.902	8	0.895	3	0.888
1162	23	0.835	20	0.866	17	0.893
1184	22	0.905	19	0.890	16	0.909
1391	15	0.858	10	0.855	5	0.934
1448	28	0.847	33	0.865	38	0.860
1566	14	0.901	9	0.900	4	0.902
1793	11	0.902	6	0.906	1	0.896
1857	24	0.867	21	0.879	18	0.876
1958	29	0.849	34	0.925	39	0.869

benzo[*b*]fluoranthene

Vial number	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]
70	41	1.471	46	1.460	51	1.476
184	26	1.473	31	1.495	36	1.508
293	44	1.469	43	1.407	48	1.468
416	53	1.472	25	1.480	30	1.474
515	35	1.459	40	1.551	45	1.474
584	49	1.458	50	1.462	54	1.504
709	42	1.516	47	1.514	52	1.495
846	12	1.501	7	1.476	2	1.497
918	27	1.474	32	1.480	37	1.507
1070	13	1.509	8	1.496	3	1.478
1162	23	1.434	20	1.446	17	1.462
1184	22	1.466	19	1.441	16	1.462
1391	15	1.505	10	1.431	5	1.508
1448	28	1.459	33	1.486	38	1.470
1566	14	1.517	9	1.502	4	1.492
1793	11	1.505	6	1.541	1	1.503
1857	24	1.417	21	1.432	18	1.438
1958	29	1.451	34	1.579[a]	39	1.512

[a]: outlier on a 95 % confidence level

Annex A: Results of the homogeneity study, ERM-CZ100

benzo[*k*]fluoranthene

Vial number	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]
70	41	0.675	46	0.683	51	0.692
184	26	0.656	31	0.673	36	0.658
293	44	0.671	43	0.654	48	0.680
416	53	0.674	25	0.680	30	0.677
515	35	0.651	40	0.714	45	0.656
584	49	0.689	50	0.663	54	0.679
709	42	0.674	47	0.663	52	0.689
846	12	0.682	7	0.671	2	0.677
918	27	0.660	32	0.647	37	0.708
1070	13	0.710	8	0.687	3	0.687
1162	23	0.651	20	0.678	17	0.668
1184	22	0.680	19	0.661	16	0.675
1391	15	0.699	10	0.653	5	0.694
1448	28	0.655	33	0.657	38	0.654
1566	14	0.705	9	0.687	4	0.681
1793	11	0.700	6	0.715	1	0.694
1857	24	0.658	21	0.659	18	0.658
1958	29	0.636	34	0.704	39	0.683

benzo[*j*]fluoranthene

Vial number	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]
70	41	0.770	46	0.784	51	0.799
184	26	0.757	31	0.772	36	0.775
293	44	0.773	43	0.747	48	0.786
416	53	0.767	25	0.783	30	0.785
515	35	0.752	40	0.781	45	0.752
584	49	0.757	50	0.725	54	0.770
709	42	0.765	47	0.768	52	0.781
846	12	0.785	7	0.769	2	0.769
918	27	0.766	32	0.729	37	0.785
1070	13	0.787	8	0.794	3	0.780
1162	23	0.712	20	0.750	17	0.769
1184	22	0.739	19	0.732	16	0.788
1391	15	0.742	10	0.762	5	0.733
1448	28	0.730	33	0.815	38	0.729
1566	14	0.822	9	0.722	4	0.737
1793	11	0.789	6	0.810	1	0.774
1857	24	0.762	21	0.771	18	0.771
1958	29	0.716	34	0.825	39	0.740

Annex A: Results of the homogeneity study, ERM-CZ100

benzo[*a*]pyrene

Vial number	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]
70	41	0.762	46	0.763	51	0.765
184	26	0.767	31	0.770	36	0.775
293[a]	44	0.732	43	0.746	48	0.737
416	53	0.758	25	0.761	30	0.763
515	35	0.769	40	0.751	45	0.753
584	49	0.764	50	0.755	54	0.756
709	42	0.756	47	0.748	52	0.754
846	12	0.763	7	0.764	2	0.777
918	27	0.775	32	0.745	37	0.781
1070	13	0.773	8	0.770	3	0.758
1162	23	0.747	20	0.777	17	0.779
1184	22	0.765	19	0.749	16	0.754
1391	15	0.777	10	0.743	5	0.768
1448	28	0.748	33	0.739	38	0.761
1566	14	0.752	9	0.769	4	0.771
1793	11	0.751	6	0.782	1	0.732
1857	24	0.747	21	0.751	18	0.755
1958	29	0.751	34	0.783	39	0.746

[a]: outlier on a 95 % confidence level

indeno[1,2,3-*cd*]pyrene

Vial number	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]
70	41	1.185	46	1.180	51	1.175
184	26	1.160	31	1.180	36	1.165
293	44	1.179	43	1.141	48	1.179
416	53	1.194	25	1.211	30	1.198
515	35	1.154	40	1.210	45	1.205
584	49	1.233	50	1.176	54	1.195
709	42	1.190	47	1.171	52	1.184
846	12	1.219	7	1.189	2	1.183
918	27	1.209	32	1.151	37	1.196
1070	13	1.223	8	1.190	3	1.209
1162	23	1.095[a]	20	1.162	17	1.207
1184	22	1.207	19	1.194	16	1.206
1391	15	1.190	10	1.213	5	1.213
1448	28	1.153	33	1.172	38	1.191
1566	14	1.170	9	1.200	4	1.213
1793	11	1.182	6	1.184	1	1.165
1857	24	1.150	21	1.191	18	1.202
1958	29	1.180	34	1.253	39	1.249

[a]: outlier on a 95 % confidence level

dibenzo[*ah*]anthracene

Vial number	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]
70	41	0.304	46	0.306	51	0.304
184	26	0.276	31	0.284	36	0.290
293	44	0.293	43	0.298	48	0.296
416	53	0.296	25	0.301	30	0.294
515	35	0.295	40	0.305	45	0.317
584	49	0.309	50	0.288	54	0.302
709	42	0.294	47	0.293	52	0.299
846	12	0.310	7	0.298	2	0.306
918	27	0.300	32	0.285	37	0.279
1070	13	0.317	8	0.293	3	0.298
1162	23	0.280	20	0.288	17	0.310
1184	22	0.306	19	0.294	16	0.304
1391	15	0.309	10	0.291	5	0.308
1448	28	0.289	33	0.283	38	0.285
1566	14	0.301	9	0.295	4	0.303
1793	11	0.302	6	0.305	1	0.313
1857	24	0.290	21	0.301	18	0.311
1958	29	0.279	34	0.318	39	0.300

Sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene

Vial number	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]	Sequence number	Result [mg/kg]
70	41	2.917	46	2.927	51	2.937
184	26	2.886	31	2.941	36	2.882
293	44	2.913	43	2.808	48	2.953
416	53	2.913	25	2.943	30	2.965
515	35	2.862	40	3.046	45	2.943
584	49	2.904	50	2.850	54	3.000
709	42	2.956	47	2.945	52	2.945
846	12	2.968	7	2.915	2	2.899
918	27	2.901	32	2.856	37	2.925
1070	13	3.006	8	2.988	3	2.935
1162	23	2.798	20	2.874	17	2.802
1184	22	2.885	19	2.834	16	2.909
1391	15	2.945	10	2.846	5	2.971
1448	28	2.844	33	2.853	38	2.867
1566	14	3.045	9	2.911	4	2.934
1793	11	2.982	6	3.066	1	2.937
1857	24	2.837	21	2.863	18	2.882
1958	29	2.802	34	3.108	39	2.953

Annex B: Minimum sample intake, ERM-CZ100

benzo[*a*]anthracene

Replicate #	50 mg			40 mg			30 mg		
	Vial number	Result, [mg/kg]	*s*, [mg/kg]	Vial number	Result, [mg/kg]	*s*, [mg/kg]	Vial number	Result, [mg/kg]	*s*, [mg/kg]
1	352	0.892	0.010	109	0.849	0.078	959	0.937	0.143
2		0.898			0.971			0.988	
3		0.913			0.971			1.010	
4		0.913			0.906			0.978	
5		0.910			0.801			1.311	
6		0.893			1.000			0.932	

benzo[*b*]fluoranthene

Replicate #	50 mg			40 mg			30 mg		
	Vial number	Result, [mg/kg]	*s*, [mg/kg]	Vial number	Result, [mg/kg]	*s*, [mg/kg]	Vial number	Result, [mg/kg]	*s*, [mg/kg]
1	352	1.420	0.014	109	1.395	0.097	959	1.770	0.178
2		1.426			1.536			1.647	
3		1.446			1.540			1.459	
4		1.441			1.450			1.631	
5		1.408			1.326			1.967	
6		1.425			1.575			1.554	

benzo[*k*]fluoranthene

Replicate #	50 mg			40 mg			30 mg		
	Vial number	Result, [mg/kg]	*s*, [mg/kg]	Vial number	Result, [mg/kg]	*s*, [mg/kg]	Vial number	Result, [mg/kg]	*s*, [mg/kg]
1	352	0.738	0.014	109	0.702	0.052	959	0.937	0.135
2		0.725			0.779			0.769	
3		0.729			0.767			0.673	
4		0.744			0.720			0.652	
5		0.729			0.645			0.983	
6		0.703			0.769			0.829	

benzo[*j*]fluoranthene

Replicate #	50 mg			40 mg			30 mg		
	Vial number	Result, [mg/kg]	*s*, [mg/kg]	Vial number	Result, [mg/kg]	*s*, [mg/kg]	Vial number	Result, [mg/kg]	*s*, [mg/kg]
1	352	0.791	0.011	109	0.775	0.059	959	0.937	0.155
2		0.785			0.818			0.988	
3		0.809			0.840			0.673	
4		0.778			0.763			0.652	
5		0.801			0.685			0.983	
6		0.789			0.839			0.932	

Annex B: Minimum sample intake, ERM-CZ100

benzo[*a*]pyrene

Replicate #	50 mg			40 mg			30 mg		
	Vial number	Result, [mg/kg]	*s*, [mg/kg]	Vial number	Result, [mg/kg]	*s*, [mg/kg]	Vial number	Result, [mg/kg]	*s*, [mg/kg]
1	352	0.749	0.009	109	0.736	0.039	959	0.937	0.143
2		0.768			0.770			0.879	
3		0.760			0.761			0.673	
4		0.773			0.738			0.652	
5		0.755			0.672			0.983	
6		0.765			0.782			0.932	

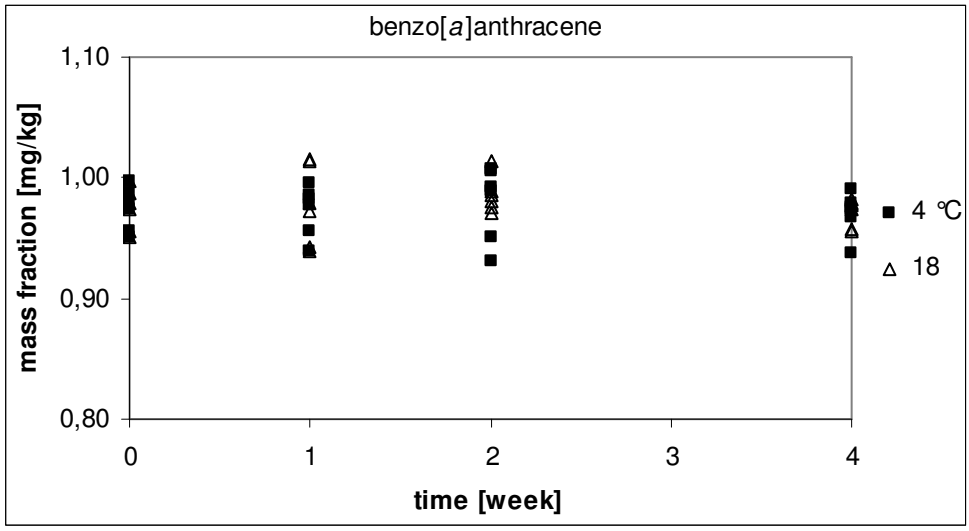
indeno[123-*c,d*]pyrene

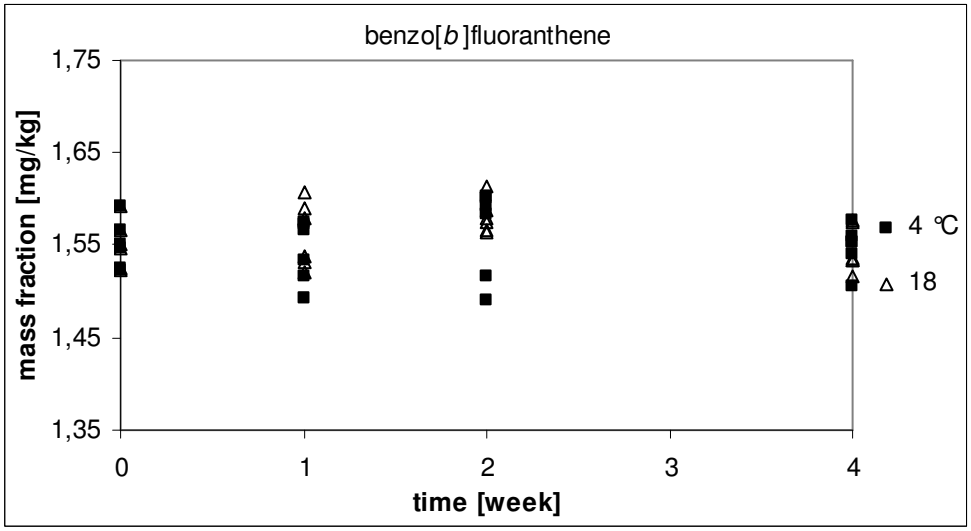
Replicate #	50 mg			40 mg			30 mg		
	Vial number	Result, [mg/kg]	*s*, [mg/kg]	Vial number	Result, [mg/kg]	*s*, [mg/kg]	Vial number	Result, [mg/kg]	*s*, [mg/kg]
1	352	1.216	0.017	109	1.194	0.112	959	1.770	0.203
2		1.251			1.345			1.647	
3		1.215			1.344			1.347	
4		1.226			1.205			1.631	
5		1.199			1.091			1.967	
6		1.228			1.372			1.554	

dibenzo[*a,h*]anthracene

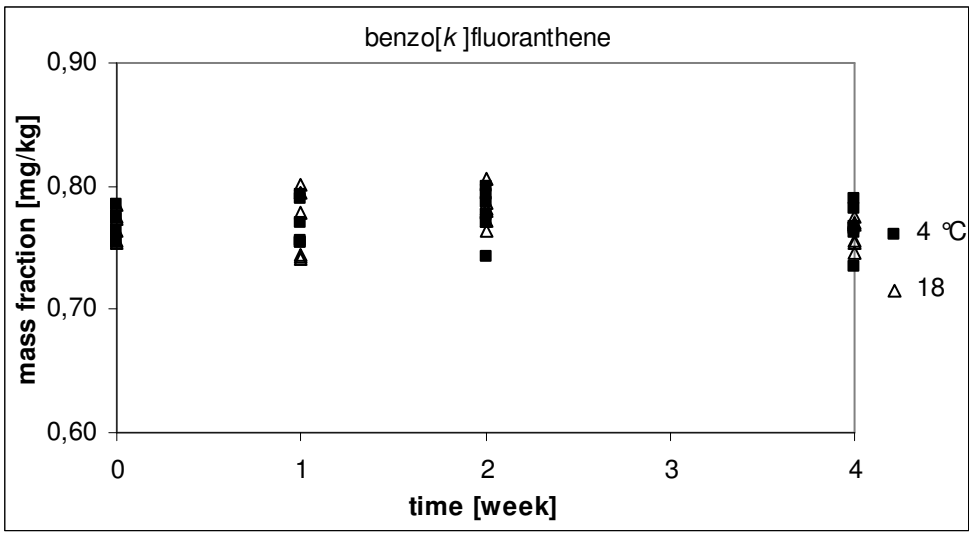
Replicate #	50 mg			40 mg			30 mg		
	Vial number	Result, [mg/kg]	*s*, [mg/kg]	Vial number	Result, [mg/kg]	*s*, [mg/kg]	Vial number	Result, [mg/kg]	*s*, [mg/kg]
1	352	0.258	0.005	109	0.294	0.023	959	0.312	0.010
2		0.267			0.320			0.329	
3		0.261			0.305			0.337	
4		0.262			0.280			0.326	
5		0.268			0.269			0.328	
6		0.255			0.330			0.311	

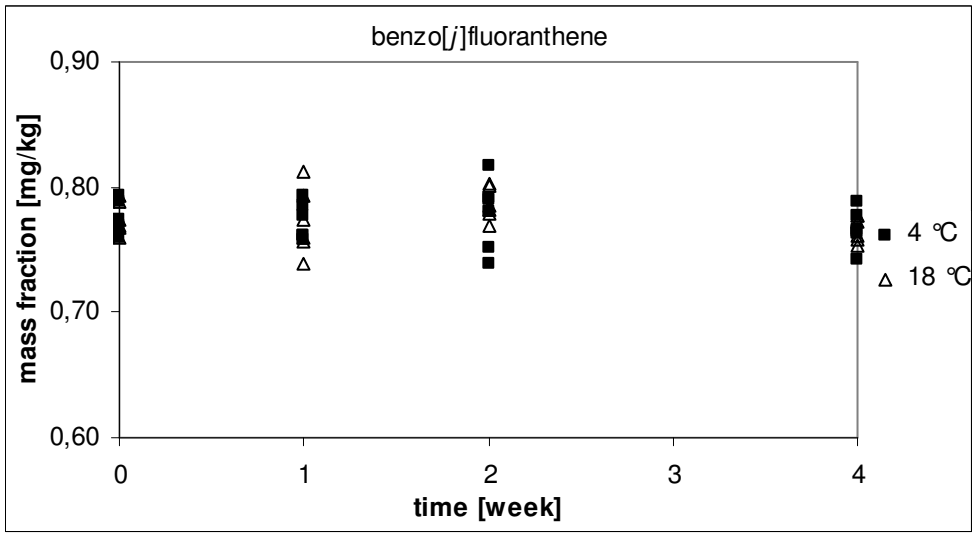
Annex C: Results of the short-term stability study, ERM-CZ100

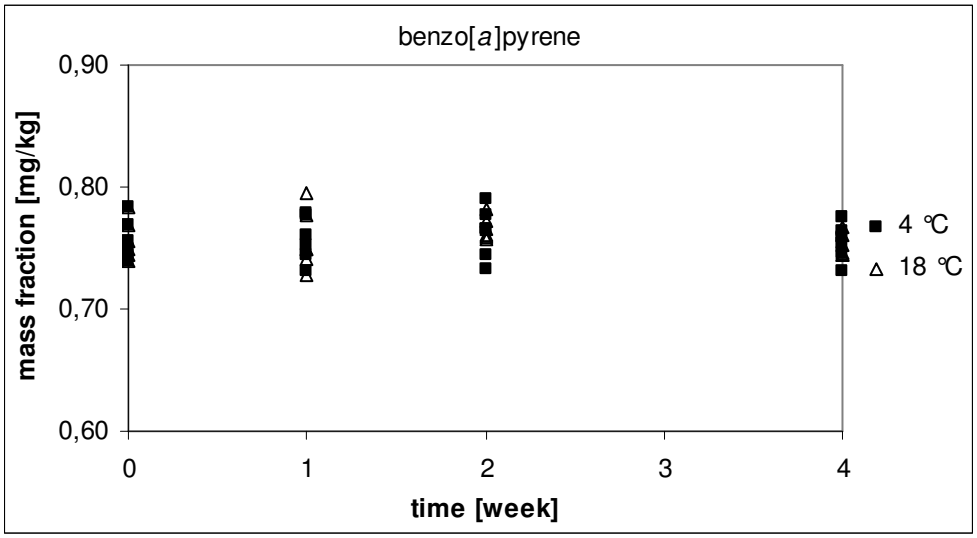




Annex C: Results of the short-term stability study, ERM-CZ100



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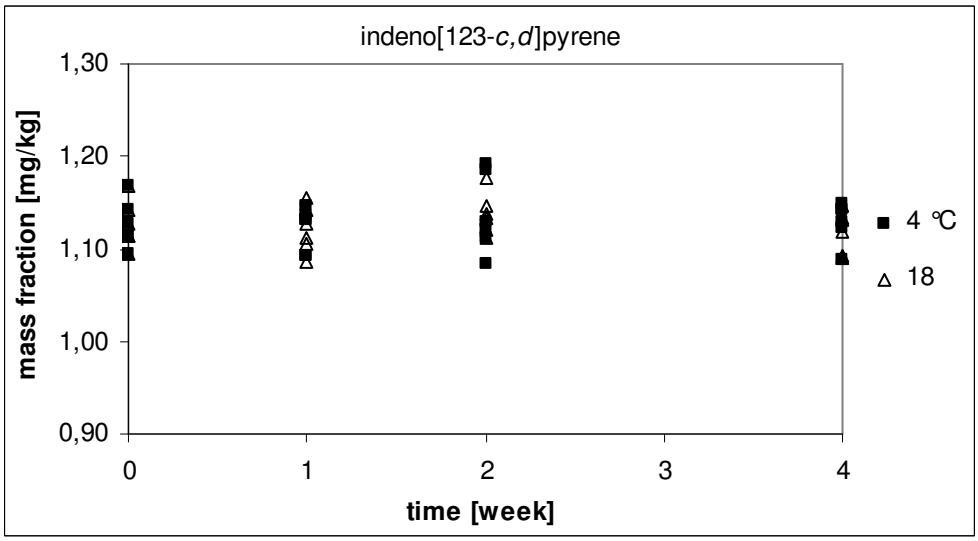
0,80
0,70
0,60
0
1
2
3
4
time [week]
4 °C
18 °C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mass fraction [mg/kg]
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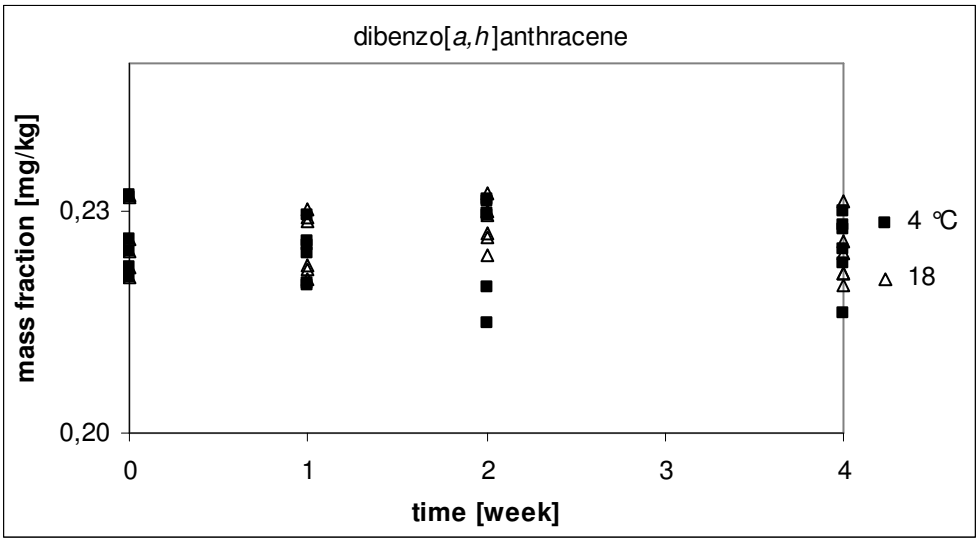
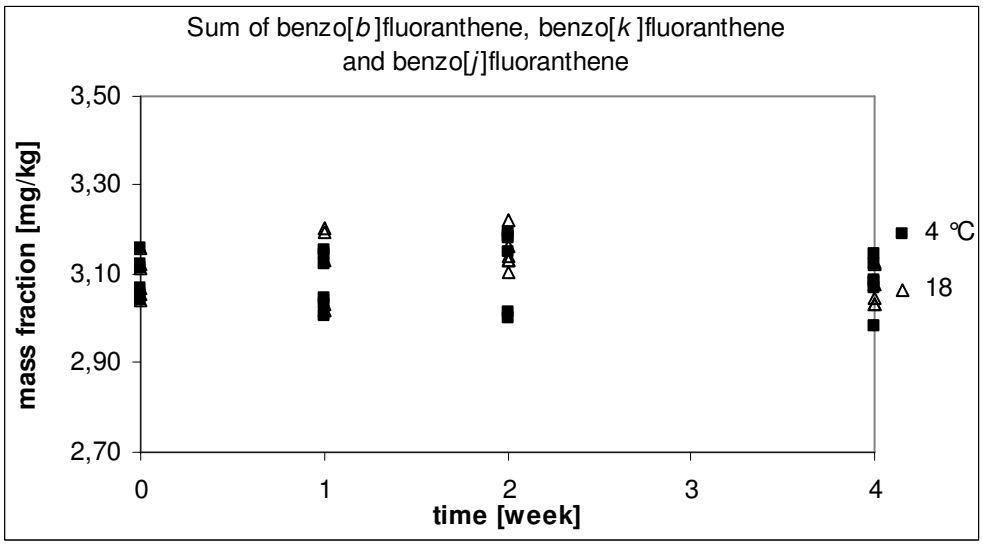
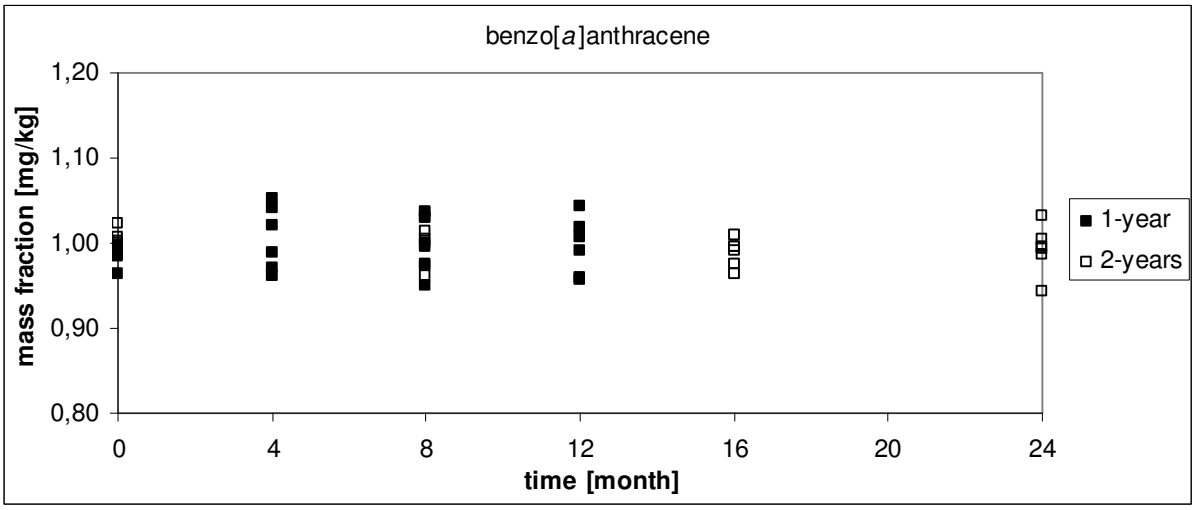
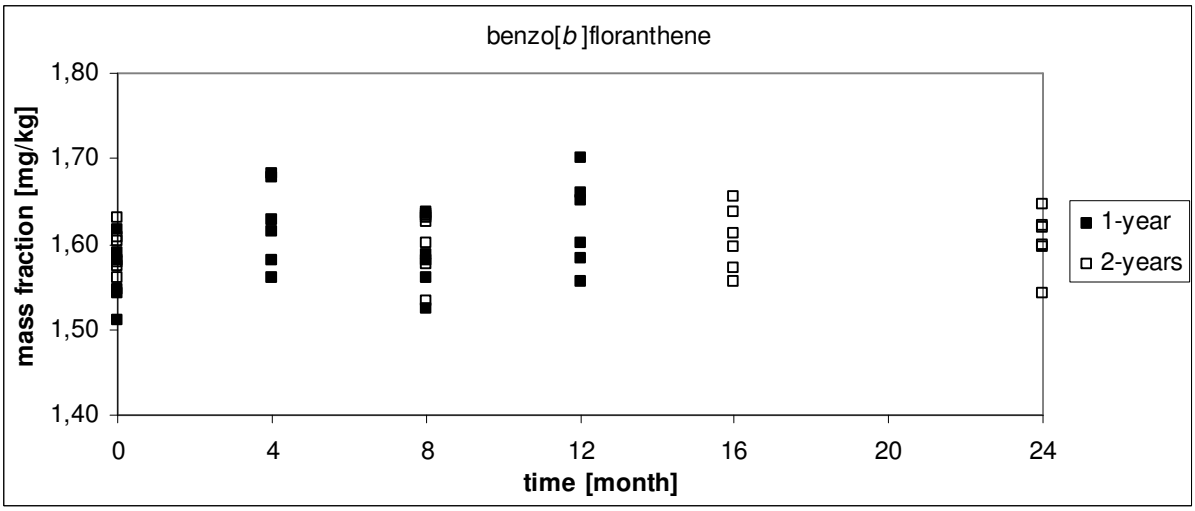
1,20
1,10
1,00
0,90
0
1
2
3
4
time [week]
4 °C
18


dibenzo[a,h]anthracene
mass fraction [mg/kg]
0,23
0,20
0
1
2
3
4
time [week]
4 °C
18

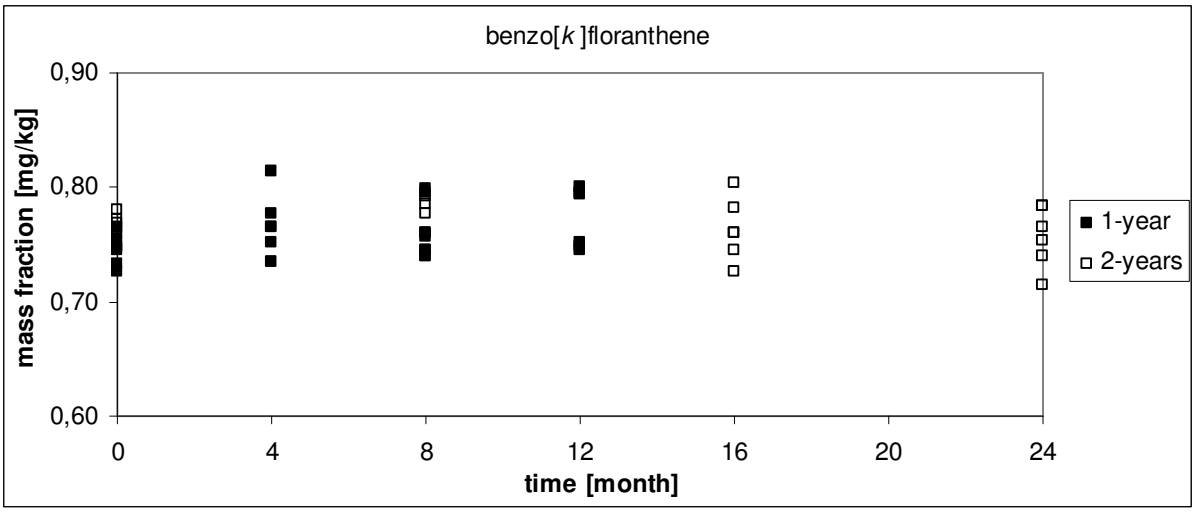

Sum of benzo[b]fluoranthene, benzo[k]fluoranthene
and benzo[j]fluoranthene
mass fraction [mg/kg]
3,50
3,30
3,10
2,90
2,70
0
1
2
3
4
time [week]
4 °C
18

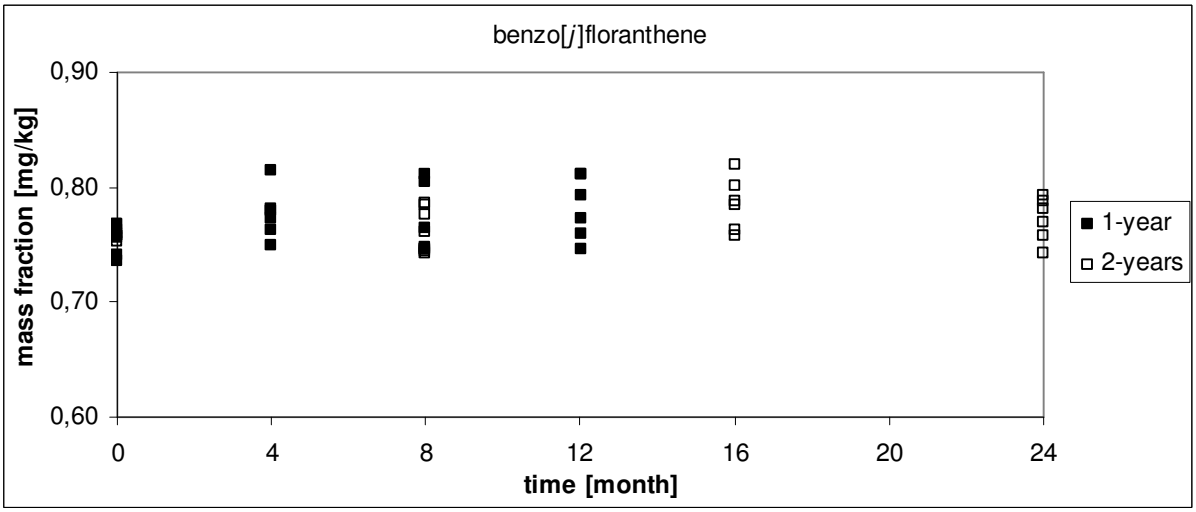
Annex D: Results of the long-term stability study, ERM-CZ100



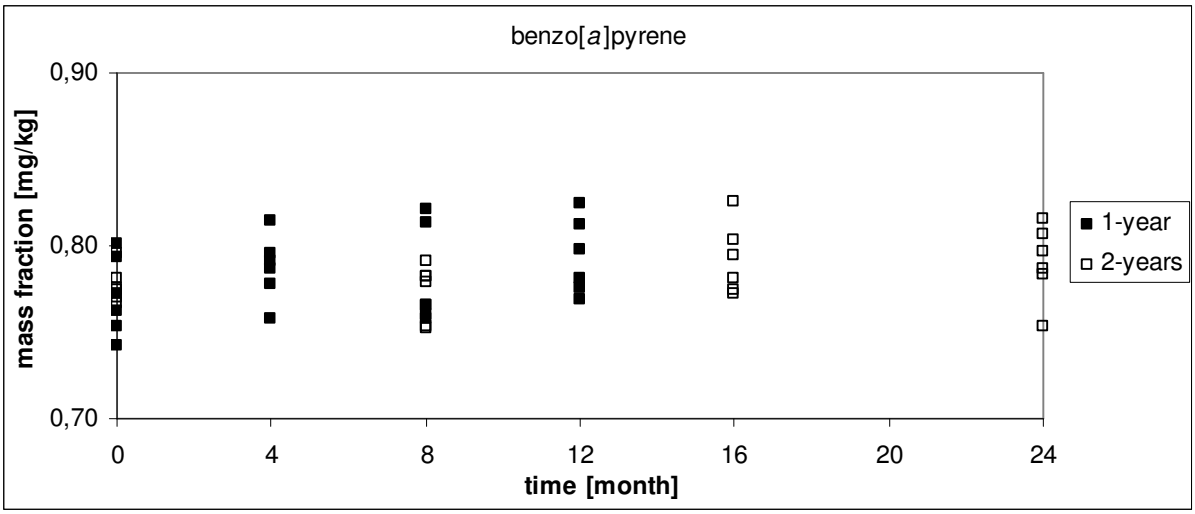


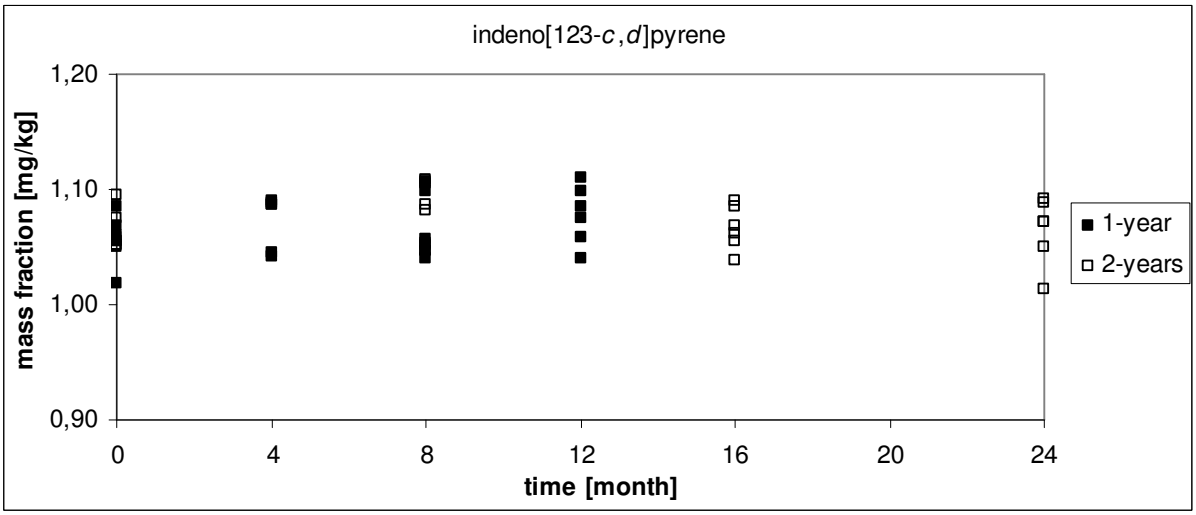
Annex D: Results of the long-term stability study, ERM-CZ100

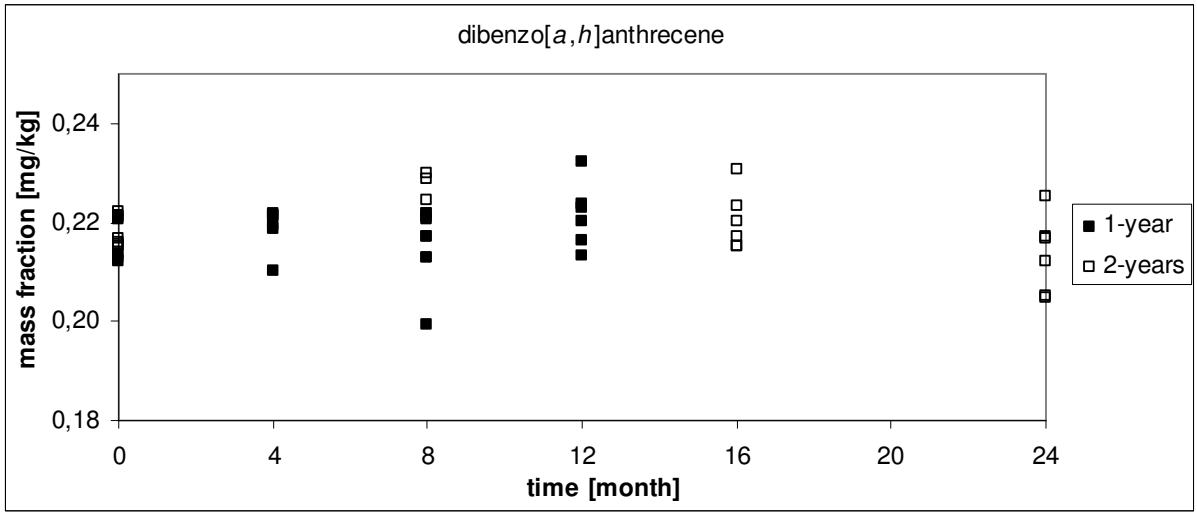


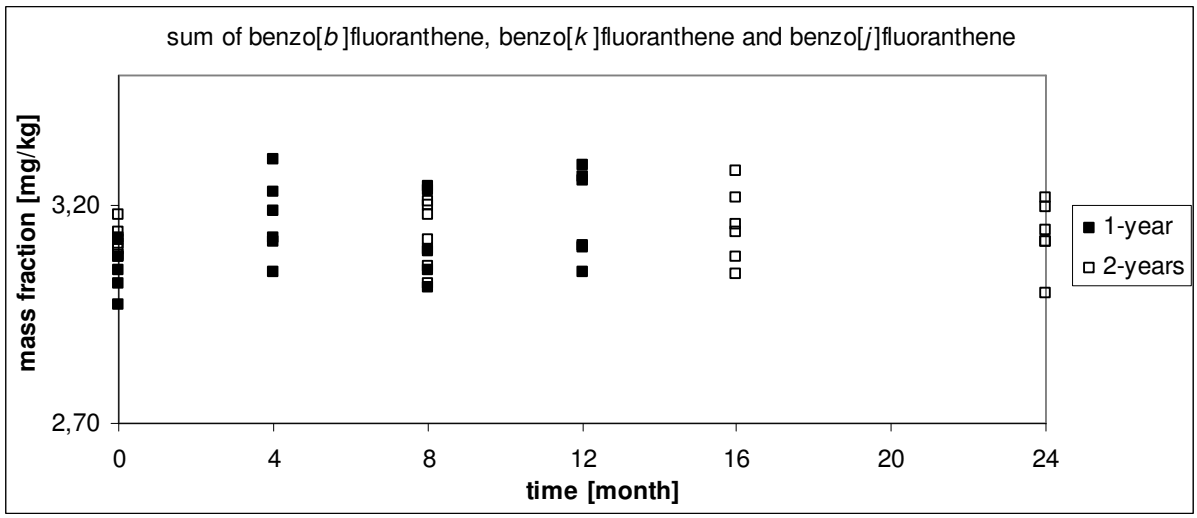


Annex D: Results of the long-term stability study, ERM-CZ100






dibenzo[a,h]anthrecene
mass fraction [mg/kg]
0,24
0,22
0,20
0,18
0
4
8
12
16
20
24
time [month]
1-year
2-years


sum of benzo[b]fluoranthene, benzo[k]fluoranthene and benzo[j]fluoranthene
mass fraction [mg/kg]
3,20
2,70
0
4
8
12
16
20
24
time [month]
1-year
2-years

Annex E: Characterisation study – laboratories and methods, ERM-CZ100

Lab-method code	PAHs	Sample mass [g]	Sample preparation	Sample clean-up	Calibrants	Instrumentation and measurement method
L01(GC/MS)	benzo[*a*]pyrene indeno[123-*c,d*]pyrene dibenzo[*a,h*]anthracene sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene	0.05302 – 0.0707	Microwave extraction with hexane-acetone (1:1 v/v).	SPE cartridges (Silica, 1 g, 6 mL) Elution: hexane-dichloromethane (2:3 v/v).	Individual standards of PAHs produced by Dr. Ehrenstorfer.	Instrument: Agilent Technologies, 6890N/5975B; Column: DB5-MS UI (30 m × 0.25 mm × 0.25 µm); Injection type: Pulsed splitless Detector: Quadrupole MS Internal calibration was used. As the internal standards deuterated PAHs produced by Dr. Ehrenstorfer were used.
L02(GC/MS)	benzo[*a*]anthracene benzo[*b*]fluoranthene benzo[*k*]fluoranthene benzo[*a*]pyrene indeno[123-*c,d*]pyrene dibenzo[*a,h*]anthracene **and additional compounds:** phenanthrene fluoranthene pyrene chrysene benzo[*g,h,i*]perylene	0.1378 – 0.1918	Soxhlet extraction with cyclohexane for 20 h	Silica-gel columns. Elution cyclohexane/dichloromethane (1:1 v/v).	Mixture of PAHs standards in a solution produced by Cerilliant Reference Standards.	Instrument: Agilent Technologies, 6890N/5975B; Column: HP5-MS (30 m × 0.25 mm × 0.25 µm); Injection type: split/splitless Detector: Quadrupole MS Internal calibration was used. As the internal standards deuterated PAHs produced by Ultra Scientific were used.
L03(HPLC/FLD)	benzo[*a*]anthracene benzo[*b*]fluoranthene benzo[*k*]fluoranthene benzo[*j*]fluoranthene benzo[*a*]pyrene indeno[123-*c,d*]pyrene sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene **and additiona compound:** coronene	0.04894 – 0.05298	Ultrasonic extraction with toluene for 15 min.	Chromatography columns (Florisil 500 mg). Elution with toluene.	Individual standards of PAHs supplied by Ultra Scientific.	Instrument: Agilent Technologies 1200 Series Column: MZ-PAH C18 3 µm (0.15 m × 3 mm). External calibration method was used. In order to control the extraction efficiency 6-methylchrysene was added before extraction step.
L04(HPLC/FLD)	benzo[*a*]anthracene benzo[*b*]fluoranthene benzo[*k*]fluoranthene benzo[*j*]fluoranthene benzo[*a*]pyrene indeno[123-*c,d*]pyrene dibenzo[*a,h*]anthracene sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene **and additional compounds:**	0.1022 – 0.1119	Accelerated solvent extraction with dichloromethane.	No clean-up step	Mixture of PAHs standards in a solution produced by Dr. Ehrenstorfer.	Instrument: Dionex RF2000 Column: supelco C18 5 µm (0.25 m × 4.6 mm). Internal calibration was used. As the internal standard 6-methylchrysene was used.

	phenanthrene anthracene fluoranthene pyrene chrysene benzo[*g,h,i*]perylene					
L05(GC/MS)	benzo[*a*]anthracene benzo[*a*]pyrene indeno[123-*c,d*]pyrene dibenzo[*a,h*]anthracene **and additional compounds:** phenantrene anthracene fluoranthene pyrene chrysene/triphenylene benzo[*g,h,i*]perylene	0.0203 – 0.0534	Soxhlet extraction with dichloromethane for 16 h	Florisil SPE. Elution: no information	Individual standards of PAHs supplied by Supelco	Instrument: Agilent 6890N GC with 5973 Network MS; Column: J&W scientific DB-5MS UI with 5 meters deactivated pre-column (50 m × 0.25 mm × 0.25 µm); Injection type: splitless Detector: Quadrupole MS Internal calibration was used. As the internal standards deuterated PAHs produced by Dr. Ehrenstorfer were used.
L06(HPLC/FLD)	benzo[*a*]anthracene benzo[*a*]pyrene indeno[123-*c,d*]pyrene dibenzo[*a,h*]anthracene sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene **and additional compounds:** naphthalene acenaphthene fluorene phenanthrene anthracene fluoranthene pyrene chrysene benzo[*g,h,i*]perylene	0.05015 – 0.05075	Accelerated Solvent Extraction with dichloromethane	No clean-up step	SRM NIST 1647e Priority Pollutant PAH was used for calibration	Instrument: Waters Acquity UPLC with Binary Solvent Manager + Sample Manager + FLR Detector. Column: ZORBAX Eclipse PAH Rapid Resolution HT 1.8 Micron 600 bar 5 µm (0.05 m × 2.1 mm). External calibration method was used.
L07(GC/MS)	Due to technical problems laboratory did not delivered the results					
L08(HPLC/FLD)	benzo[*a*]anthracene benzo[*a*]pyrene indeno[123-*c,d*]pyrene dibenzo[*a,h*]anthracene sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene **and additional compounds:** fluoranthene phenanthrene anthracene pyrene chrysene	0.091 – 0.12	Soxhlet extraction with pentane for 24 h	No clean-up step	SRM NIST 1647e Priority Pollutant PAH was used for calibration.	Instrument: HPLC-Fluorescence, 9075 Varian , Prostar 240 Varian Column: Chromspher PAH, 5 µm C18 packed 0.1 m x 3 mm As a internal standard b,b-binapthy was used produced by Dr. Ehrenstorfen.

	benzo[*g,h,i*]perylene					
L09(HPLC/FLD)	benzo[*a*]anthracene benzo[*b*]fluoranthene benzo[*k*]fluoranthene benzo[*j*]fluoranthene benzo[*a*]pyrene indeno[123-*c,d*]pyrene dibenzo[*a,h*]anthracene	0.0505 – 0.0553	Soxhlet extraction with hexane/acetone (1:1 v/v)	Silica gel cartridges. Elution: hexane/dichloromethane (40:60 v/v)	Individual standards of PAHs produced by Cerillant or Dr. Ehrenstorfer	Instrument: HPLC system Varian ProStar; Column: ChromSpher 5 PAH 5 µm (0.15 m × 4.6 mm)
L10(GC/MS)	benzo[*a*]anthracene benzo[*a*]pyrene indeno[123-*c,d*]pyrene dibenzo[*a,h*]anthracene sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene	0.05003 – 0.15093	Soxhlet extraction with toluene for 8 h	Silica Gel columns. Elution: hexane/toluene (7:3 v/v)	Individual standards of PAHs supplied by Dr. Ehrenstorfer	Instrument: Thermo Finnigan - trace DSQ Column: HP-5 (30 m × 0.25 mm × 0.25 µm) External calibration method was used
L011(GC/MS)	benzo[*a*]anthracene benzo[*a*]pyrene indeno[123-*c,d*]pyrene dibenzo[*a,h*]anthracene sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene **and additional compounds:** phenanthrene	0.10025 – 0.10827	Pressurized Liquid Extraction with hexane/dichloromethane (1:1 v/v)	Clean up with Na_2SO_4 in extract cell	Individual standards of PAHs supplied by Dr. Ehrenstorfer	Instrument: Agilent 6890N Column: 8% Phenyl Polycarborane-siloxane (50 m × 0.22 mm × 0.25 µm) Injection type: split/splitless Detector: Quadrupole MS (Agilent 5975B) Internal calibration was used. As the internal standards deuterated PAHs produced by CIL CERILLIANT were used.
L12(GC/MS)	benzo[*a*]anthracene benzo[*b*]fluoranthene benzo[*k*]fluoranthene benzo[*j*]fluoranthene benzo[*a*]pyrene indeno[123-*c,d*]pyrene sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene	0.099786 – 0.101502	Soxhlet extraction with dichloromethane for 16 h	Glass Chromabond silica cartridges (500 mg). Elution: n-hexane/dichloromethane (4:1 v/v).	SRM NIST 2260a was used for calibration.	Instrument: Trace DSQ Column: VF-17MS (30 m × 0.25 mm × 0.25 µm); Injection type: Pulsed splitless Detector: Quadrupole MS Internal calibration was used. As the internal standards deuterated PAHs produced by CIL and Cabbridge were used.
L13(GC/MS)	benzo[*a*]anthracene benzo[*b*]fluoranthene benzo[*k*]fluoranthene benzo[*j*]fluoranthene benzo[*a*]pyrene indeno[123-*c,d*]pyrene dibenzo[*a,h*]anthracene sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene	0.0941 – 0.1142	Accelerated Solvent Extraction with dichloromethane.	Aminopropylsilane SPE cartridges. Elution: hexane/dichloromethane (1:1 v/v)	Individual standards of PAHs produced by IRMM Dr. Ehrenstorfer	Instrument: Agilent 6890GC-5973inertMSD Column: DB-17HT (30 m × 0.25 mm × 0.25 µm). Injection type: split/splitles Detector: Quadrupole MS Internal calibration was used. As the internal standards deuterated PAHs produced by Dr. Ehrenstorfer were used
L14(GC/MS)	benzo[*a*]anthracene benzo[*a*]pyrene indeno[123-*c,d*]pyrene	0.00204 – 0.00457	Compounds were released from a sample using thermal desorption	No clean-up step	SRM NIST 1649a was used for calibration	Instrument: Agilent 6890GC-5973inertMSD Column: Zebron ZB5 MS (30 m ×

	dibenzo[*a,h*]anthracene sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene **and additional compounds:** anthracene fluoranthene pyrene chrysene benzo[*g,h,i*]perylene benzo[*e*]pyrene					0.25 mm × 0.25 µm). Injection type: direct transferline from MARKES thermal desorber. Detector: Quadrupole MS External calibration method was used.
L15(GC/MS)	benzo[*a*]anthracene benzo[*b*]fluoranthene benzo[*k*]fluoranthene benzo[*j*]fluoranthene benzo[*a*]pyrene indeno[123-*c,d*]pyrene sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene **and additional compounds:** phenanthrene anthracene fluoranthene pyrene chrysene benzo[*g,h,i*]perylene	0.0492 – 0.0549	Accelerated Solvent Extraction with toluene	Chromatographic column (10 g SiO2 and 5 g Al_2O_3 + 3% H_2O). Elution: hexane/dichloromethane (1:1 v/v). SPE cartridge (1 g C18-modified silica gel). Elution: acetronitrile.	Mixture of PAHs standards in a solution produced by Dr. Ehrenstorfer	Instrument: Agilent 6890GC Column: Phenomenex Zebron ZB-50 (30 m × 0.25 mm × 0.25 µm). Injection type: PTV in pulsed splitless mode Detector: High resolution sector field MS, Thermo Finnigan MAT95S Internal calibration was used. As the internal standards deuterated PAHs produced by Dr. Ehrenstorfer were used.
L16(HPLC/FLD)	benzo[*a*]anthracene benzo[*b*]fluoranthene benzo[*k*]fluoranthene benzo[*j*]fluoranthene benzo[*a*]pyrene indeno[123-*c,d*]pyrene dibenzo[*a,h*]anthracene sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene	No information	Soxhlet extraction with hexane/dichloromethane (1:1 v/v) for 4 h	Florisil columns. Elution: no information	No information	Instrument: Shimadzu UFLC XR Column: Pinnacle II 4 µm 150x3.2 mm Detector: fluorescence detector RF-10A XL
L17(HPLC/FLD)	benzo[*a*]anthracene benzo[*b*]fluoranthene benzo[*k*]fluoranthene benzo[*j*]fluoranthene benzo[*a*]pyrene indeno[123-*c,d*]pyrene dibenzo[*a,h*]anthracene sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene	0.0621 – 0.3466	Ultrasonic extraction with dichloromethane/methanol (9:1 v/v) for 30 min	No clean-up step	Mixture of PAHs standards in a solution produced by ULTRA SCIENTIFIC Analytical Solutions and Dr.Ehrenstorfer.	Instrument: HPLC Agilent Technologies 1200series Column: LiChroCART 250-3 4 µm Merck (0.25 m × 3.0 mm). External calibration method was used.
L18(HPLC/FLD)	benzo[*a*]anthracene	0.1076 –	Soxhlet extraction with	No clean-up step	Mixture of PAHs standards	Instrument: HPLC system Waters

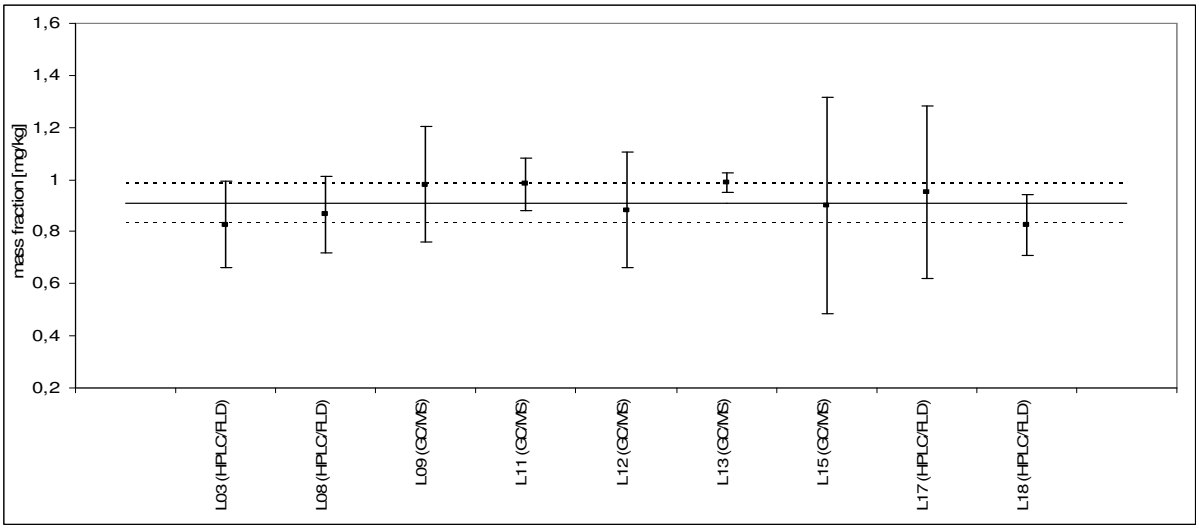
	benzo[*b*]fluoranthene benzo[*k*]fluoranthene benzo[*j*]fluoranthene benzo[*a*]pyrene indeno[123-*c,d*]pyrene dibenzo[*a,h*]anthracene sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene **and additional compounds:** phenanthrene anthracene fluoranthene pyrene chrysene benzo[*g,h,i*]perylene	0.1785	dichloromethane/methanol (9:1 v/v) for 3 h	in a solution produced by Cerilliant and Supelco	LCM Module; FLD Waters 474; Column: Bakerbond PAH Plus 5 µm (0.25 m × 3.0 mm). External calibration method was used.

benzo[*a*]anthracene

Lab-method code	Individual results[a]						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L03(GC/MS)	0.84	0.88	0.79	0.83	0.81	0.81	0.83	0.03	0.17
L08(HPLC/FLD)	0.84	0.82	0.88	0.92	0.89	0.84	0.87	0.04	0.15
L09(HPLC/FLD)	1.04	1.08	0.8	0.99	1.01	0.97	0.98	0.10	0.22
L11(GC/MS)	0.921	0.997	1.004	1.027	0.942	1.007	0.983	0.042	0.100
L12(GC/MS)	0.88	0.94	0.93	0.82	0.86	0.87	0.88	0.05	0.22
L13(GC/MS)	0.978	0.969	1.027	0.981	0.968	1.008	0.989	0.024	0.037
L15(GC/MS)	0.96	0.94	0.88	0.89	0.85	0.87	0.90	0.04	0.42
L17(HPLC/FLD)	1.013	1.004	0.940	0.946	0.938	0.870	0.952	0.052	0.330
L18(HPLC/FLD)	0.814	0.852	0.834	0.830	0.796	0.821	0.825	0.019	0.116

[a]: values reported on mass of the sample after conditioning the sample using conditions as described in EN12341

Error bars in the graph represent expanded uncertainties (U_{Lab}) as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Excluded results were not used for the calculation of the certified value.

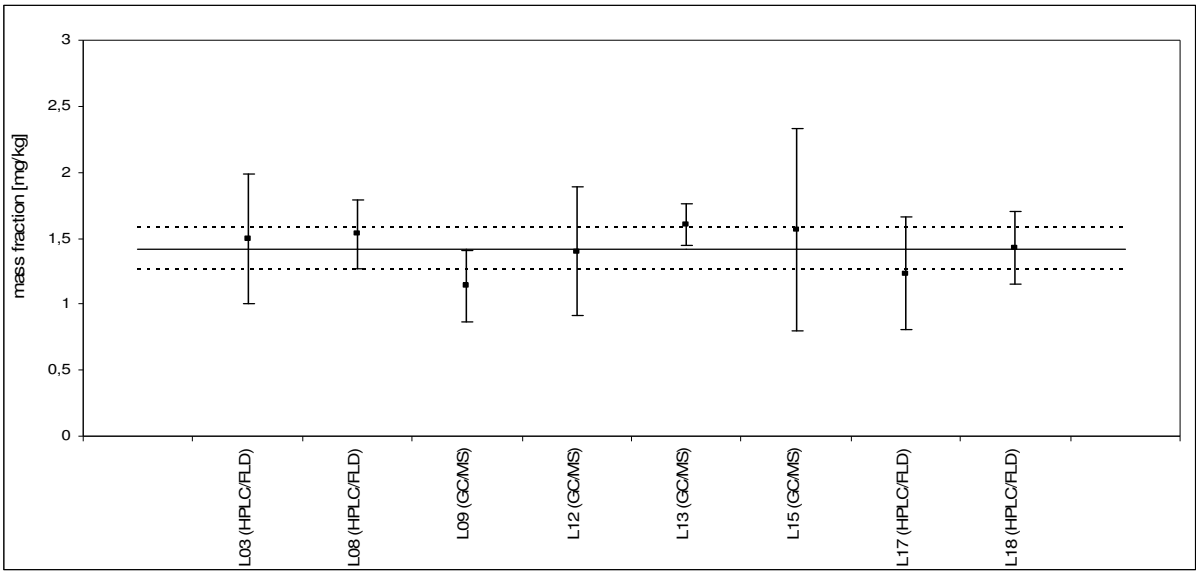
Lab-method code	Excluded results						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L01(GC/MS)	1.16	1.06	1.06	0.95	1.08	1.03	1.06	0.07	0.11
L02(GC/MS)	1.46	1.39	1.25	1.3	1.25	1.26	1.32	0.09	0.16
L04(HPLC/FLD)	0.81	0.85	0.81	0.81	0.83	0.83	0.82	0.02	0.12
L05(GC/MS)	0.89	0.97	0.91	0.97	0.96	0.78	0.91	0.07	0.18
L06(HPLC/FLD)	1.05	1.06	1.05	0.86	0.81	0.84	0.95	0.12	0.05
L10(GC/MS)	0.515	0.53	0.38	0.484	0.657	0.453	0.503	0.092	0.350
L14(GC/MS)	0.68	0.72	0.66	0.78	0.69	0.66	0.70	0.05	0.06
L16(HPLC/FLD)	1.033	1.066	0.929	0.94	0.937	0.91	0.969	0.064	0.415

benzo[*b*]fluoranthene

Lab-method code	Individual results[a]						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L03(GC/MS)	1.54	1.52	1.48	1.48	1.53	1.43	1.50	0.04	0.50
L08(HPLC/FLD)	1.5	1.5	1.5	1.5	1.6	1.6	1.5	0.1	0.3
L09(HPLC/FLD)	1.11	1.09	1.01	1.36	1.13	1.12	1.14	0.12	0.27
L12(GC/MS)	1.3	1.4	1.4	1.4	1.5	1.4	1.4	0.1	0.5
L13(GC/MS)	1.569	1.562	1.672	1.562	1.579	1.665	1.602	0.052	0.156
L15(GC/MS)	1.58	1.57	1.56	1.53	1.57	1.57	1.56	0.02	0.77
L17(HPLC/FLD)	1.321	1.287	1.228	1.292	1.169	1.106	1.234	0.083	0.430
L18(HPLC/FLD)	1.381	1.487	1.464	1.423	1.380	1.430	1.428	0.043	0.274

[a]: values reported on mass of the sample after conditioning the sample using conditions as described in EN12341

Error bars in the graph represent expanded uncertainties (U_{Lab}) as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Excluded results were not used for the calculation of the certified value.

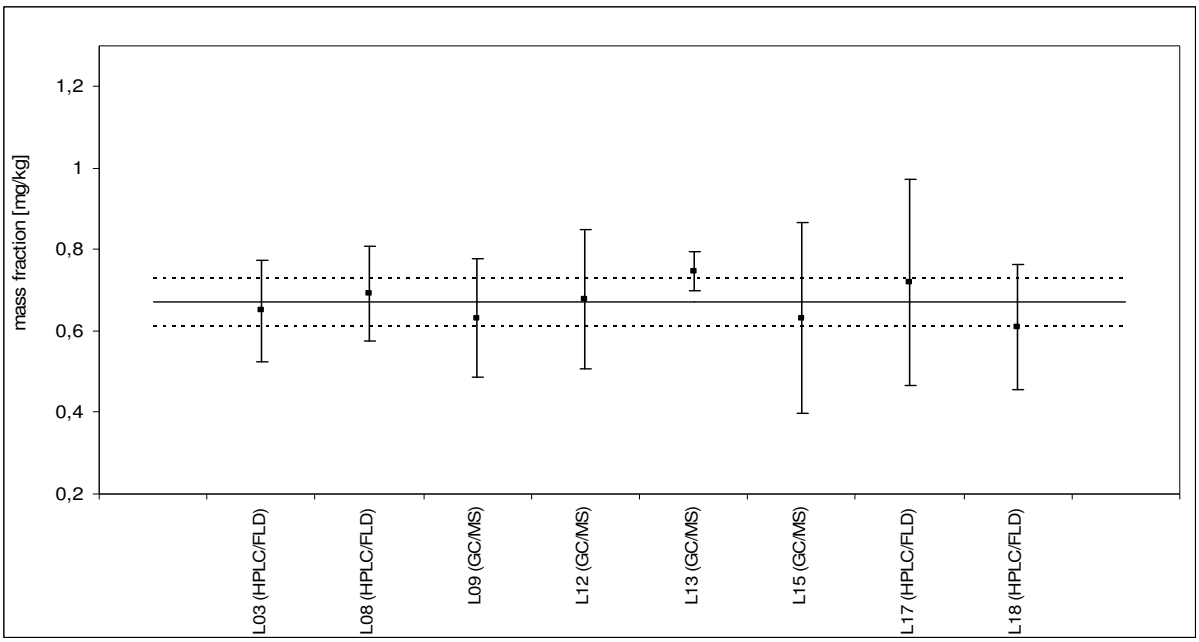
Lab-method code	Excluded results						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L02(GC/MS)	1.82	1.83	1.73	2.02	1.93	1.78	1.85	0.11	0.43
L04(HPLC/FLD)	1.72	1.81	1.78	1.72	1.81	1.82	1.78	0.05	0.27
L16(HPLC/FLD)	1.06	1.083	1.055	1.065	0.941	0.854	1.010	0.092	0.180

benzo[*k*]fluoranthene

Lab-method code	Individual results[a]						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L03(GC/MS)	0.66	0.68	0.64	0.65	0.65	0.62	0.65	0.02	0.13
L08(HPLC/FLD)	0.69	0.65	0.69	0.69	0.74	0.69	0.69	0.03	0.12
L09(HPLC/FLD)	0.62	0.62	0.58	0.75	0.60	0.62	0.63	0.06	0.15
L12(GC/MS)	0.70	0.74	0.69	0.66	0.62	0.66	0.68	0.04	0.17
L13(GC/MS)	0.725	0.726	0.796	0.747	0.724	0.762	0.747	0.029	0.049
L15(GC/MS)	0.63	0.64	0.61	0.65	0.62	0.64	0.63	0.01	0.24
L17(HPLC/FLD)	0.729	0.749	0.689	0.756	0.723	0.672	0.720	0.033	0.250
L18(HPLC/FLD)	0.601	0.649	0.63	0.631	0.573	0.578	0.610	0.031	0.155

[a]: values reported on mass of the sample after conditioning the sample using conditions as described in EN12341

Error bars in the graph represent expanded uncertainties (U_{Lab}) as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Excluded results were not used for the calculation of the certified value.

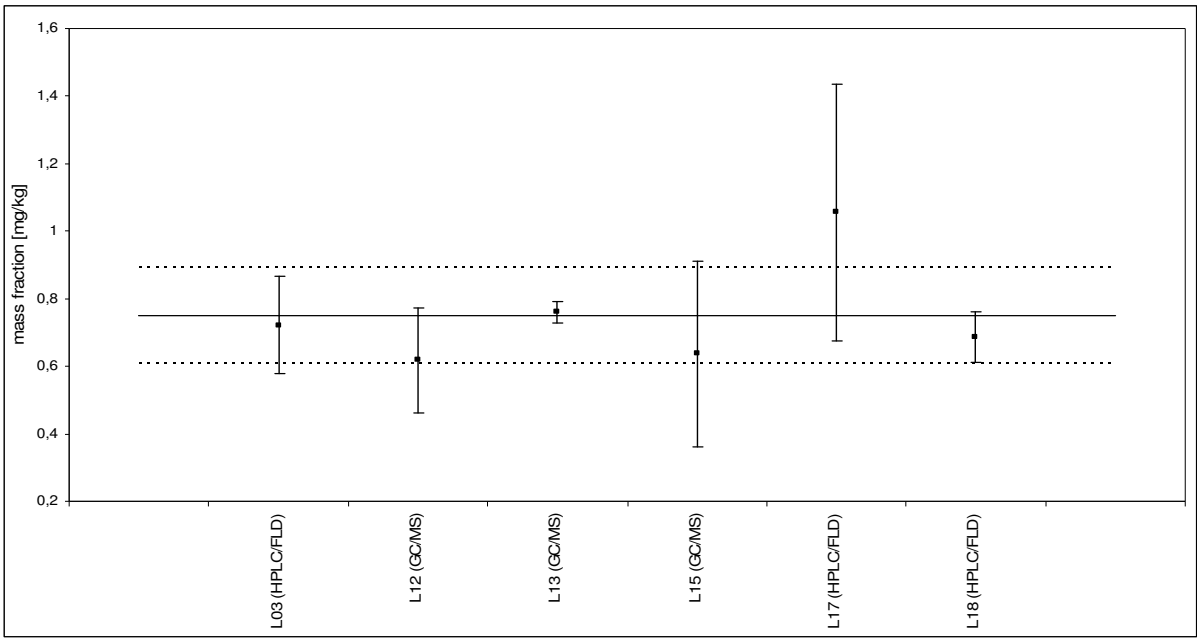
Lab-method code	Excluded results						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L02(GC/MS)	0.98	1.09	1.03	0.98	0.78	0.93	0.97	0.11	-
L04(HPLC/FLD)	0.68	0.72	0.69	0.67	0.71	0.71	0.70	0.02	0.10
L16(HPLC/FLD)	0.515	0.496	0.462	0.495	0.432	0.453	0.476	0.031	0.083

benzo[*j*]fluoranthene

Lab-method code	Individual results[a]						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L03(GC/MS)	0.69	0.69	0.74	0.76	0.72	0.73	0.72	0.03	0.15
L12(GC/MS)	0.73	0.72	0.56	0.66	0.52	0.52	0.62	0.10	0.16
L13(GC/MS)	0.727	0.780	0.778	0.754	0.753	0.772	0.761	0.020	0.032
L15(GC/MS)	0.63	0.67	0.63	0.65	0.62	0.62	0.64	0.02	0.28
L17(HPLC/FLD)	1.011	0.995	1.058	1.130	1.091	1.048	1.056	0.050	0.38
L18(HPLC/FLD)	0.689	0.701	0.698	0.707	0.672	0.646	0.686	0.023	0.075

[a]: values reported on mass of the sample after conditioning the sample using conditions as described in EN12341

Error bars in the graph represent expanded uncertainties (U_{Lab}) as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Excluded results were not used for the calculation of the certified value.

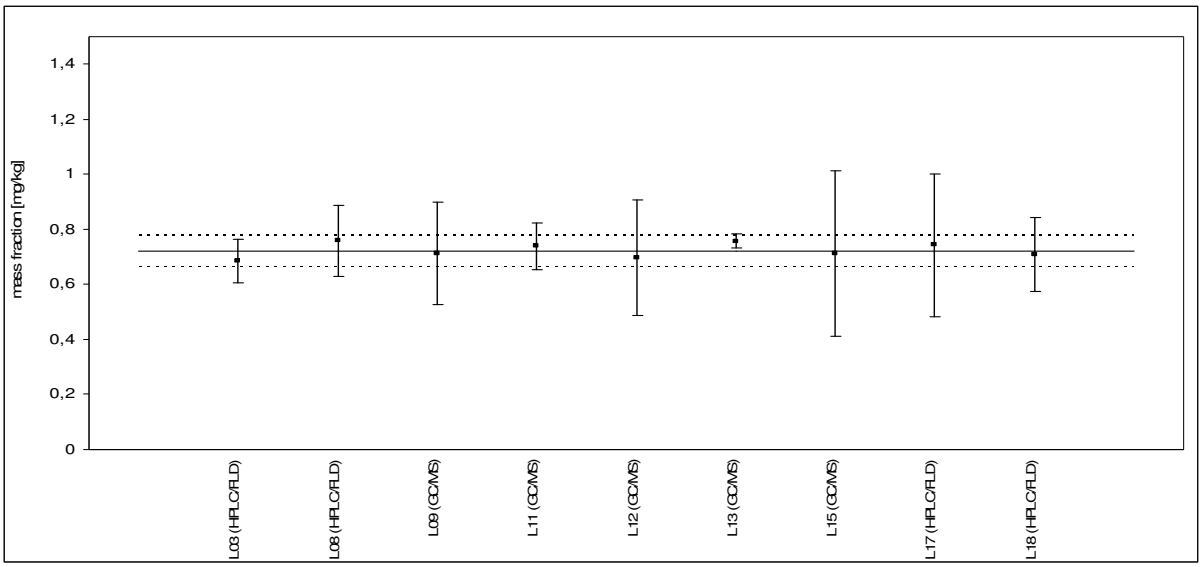
Lab-method code	Excluded results						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L04(HPLC/FLD)	0.70	0.72	0.64	0.66	0.73	0.68	0.69	0.03	0.10
L16(HPLC/FLD)	0.243	0.23	0.225	0.23	0.207	0.215	0.225	0.013	0.032

benzo[*a*]pyrene

Lab-method code	Individual results[a]						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L03(GC/MS)	0.70	0.72	0.68	0.68	0.68	0.65	0.69	0.02	0.08
L08(HPLC/FLD)	0.76	0.71	0.77	0.76	0.81	0.75	0.76	0.03	0.13
L09(HPLC/FLD)	0.71	0.68	0.65	0.76	0.71	0.76	0.71	0.04	0.19
L11(GC/MS)	0.71	0.77	0.74	0.80	0.69	0.73	0.74	0.04	0.09
L12(GC/MS)	0.71	0.67	0.69	0.70	0.71	0.69	0.70	0.02	0.21
L13(GC/MS)	0.750	0.795	0.766	0.742	0.739	0.752	0.757	0.021	0.025
L15(GC/MS)	0.71	0.74	0.73	0.71	0.71	0.67	0.71	0.02	0.30
L17(HPLC/FLD)	0.697	0.743	0.736	0.708	0.784	0.785	0.742	0.037	0.260
L18(HPLC/FLD)	0.695	0.703	0.704	0.745	0.711	0.694	0.709	0.019	0.135

[a]: values reported on mass of the sample after conditioning the sample using conditions as described in EN12341

Error bars in the graph represent expanded uncertainties (U_{Lab}) as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Excluded results were not used for the calculation of the certified value.

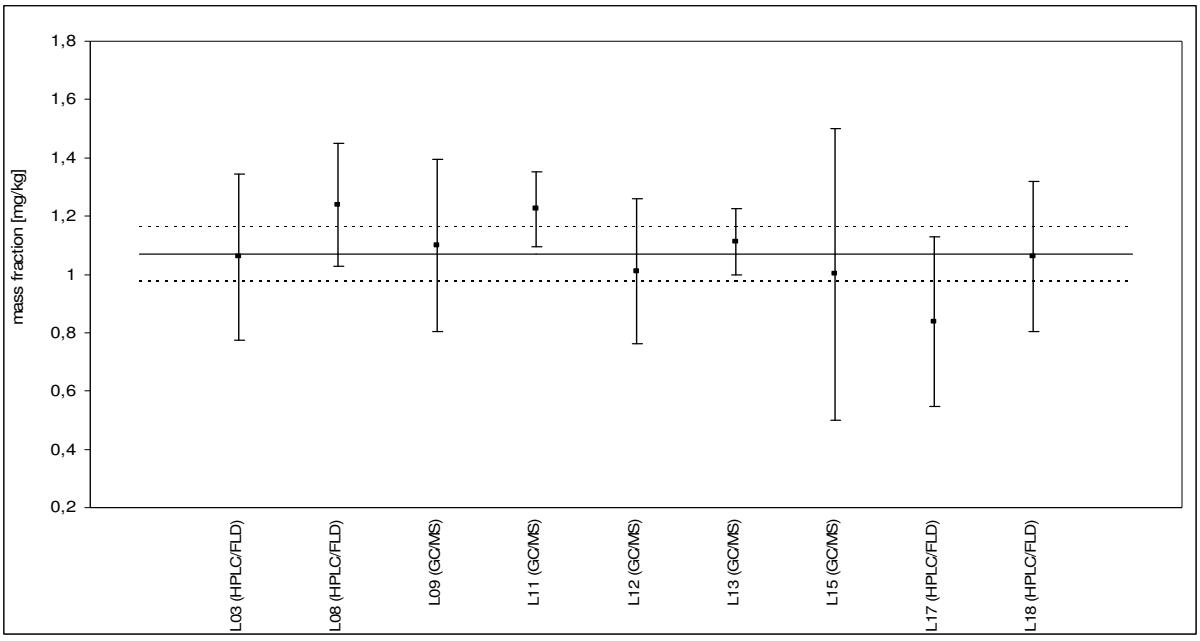
Lab-method code	Excluded results						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L01(GC/MS)	0.64	0.61	0.71	0.62	0.71	0.69	0.66	0.05	0.07
L02(GC/MS)	1.33	1.31	1.27	1.20	1.20	1.18	1.25	0.06	0.59
L04(HPLC/FLD)	0.74	0.79	0.76	0.73	0.78	0.78	0.76	0.02	0.11
L05(GC/MS)	0.52	0.58	0.60	0.54	0.58	0.57	0.57	0.03	0.07
L06(HPLC/FLD)	1.06	1.05	1.06	1.02	0.99	1.02	1.03	0.03	0.05
L10(GC/MS)	0.431	0.418	0.266	0.394	0.556	0.331	0.399	0.098	0.124
L14(GC/MS)	0.88	0.80	0.87	0.98	0.81	0.90	0.87	0.07	0.08
L16(HPLC/FLD)	0.674	0.931	0.346	0.463	0.498	0.42	0.555	0.214	0.443

indeno[123-*c,d*]pyrene

Lab-method code	Individual results[a]						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L03(GC/MS)	1.08	1.10	1.02	1.05	1.10	1.01	1.06	0.04	0.29
L08(HPLC/FLD)	1.2	1.1	1.2	1.2	1.3	1.3	1.2	0.1	0.21
L09(HPLC/FLD)	1.07	1.1	1.18	0.96	1.14	1.15	1.10	0.08	0.3
L11(GC/MS)	1.14	1.26	1.25	1.31	1.18	1.21	1.22	0.06	0.13
L12(GC/MS)	1.03	1.1	1.03	0.99	1	0.92	1.01	0.06	0.25
L13(GC/MS)	1.126	1.139	1.117	1.104	1.071	1.107	1.111	0.023	0.114
L15(GC/MS)	0.99	1.00	1.02	0.99	0.98	1.03	1.00	0.02	0.5
L17(HPLC/FLD)	0.832	0.830	0.869	0.883	0.823	0.787	0.837	0.034	0.29
L18(HPLC/FLD)	1.107	1.100	0.981	1.127	1.030	1.028	1.062	0.057	0.258

[a]: values reported on mass of the sample after conditioning the sample using conditions as described in EN12341

Error bars in the graph represent expanded uncertainties (U_{Lab}) as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Excluded results were not used for the calculation of the certified value.

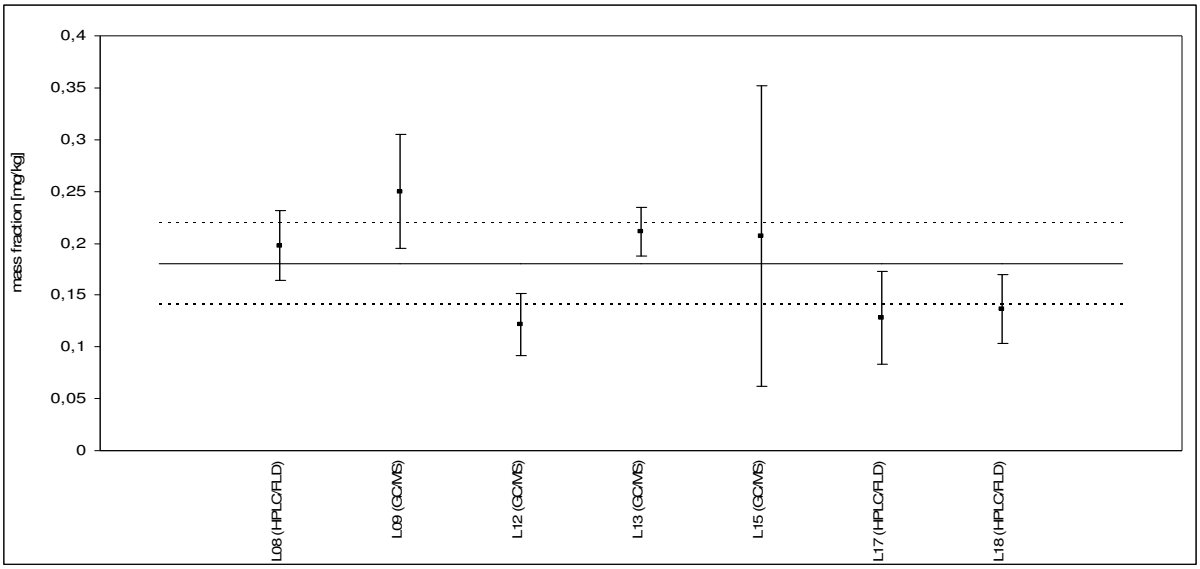
Lab-method code	Excluded results						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L01(GC/MS)	1.22	1.17	1.25	1.23	1.32	1.31	1.25	0.06	0.19
L02(GC/MS)	1.66	1.57	1.44	1.55	1.35	1.48	1.51	0.11	0.32
L04(HPLC/FLD)	0.80	0.89	0.88	0.90	0.84	0.87	0.86	0.04	0.13
L05(GC/MS)	1.14	1.50	1.31	1.19	1.50	1.02	1.28	0.20	0.34
L06(HPLC/FLD)	0.81	0.85	0.84	1.29	1.31	1.3	1.07	0.26	0.06
L10(GC/MS)	0.676	0.795	0.49	0.773	1.099	0.624	0.743	0.206	-
L14(GC/MS)	1.09	1.03	0.89	1.16	0.88	0.88	0.99	0.12	0.14
L16(HPLC/FLD)	0.584	0.543	0.435	0.307	0.301	0.368	0.423	0.120	0.154

dibenzo[*a,h*]anthracene

Lab-method code	Individual results[a]						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L08(HPLC/FLD)	0.19	0.18	0.19	0.20	0.22	0.19	0.20	0.01	0.03
L09(HPLC/FLD)	0.25	0.25	0.22	0.27	0.25	0.25	0.25	0.02	0.06
L12(GC/MS)	0.11	0.10	0.14	0.10	0.13	0.15	0.12	0.02	0.03
L13(GC/MS)	0.207	0.229	0.214	0.200	0.208	0.209	0.211	0.010	0.023
L15(GC/MS)	0.21	0.21	0.21	0.21	0.20	0.20	0.21	0.01	0.15
L17(HPLC/FLD)	0.140	0.123	0.122	0.129	0.128	0.127	0.128	0.006	0.045
L18(HPLC/FLD)	0.137	0.124	0.144	0.138	0.123	0.153	0.137	0.012	0.033

[a]: values reported on mass of the sample after conditioning the sample using conditions as described in EN12341

Error bars in the graph represent expanded uncertainties (U_{Lab}) as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Excluded results were not used for the calculation of the certified value.

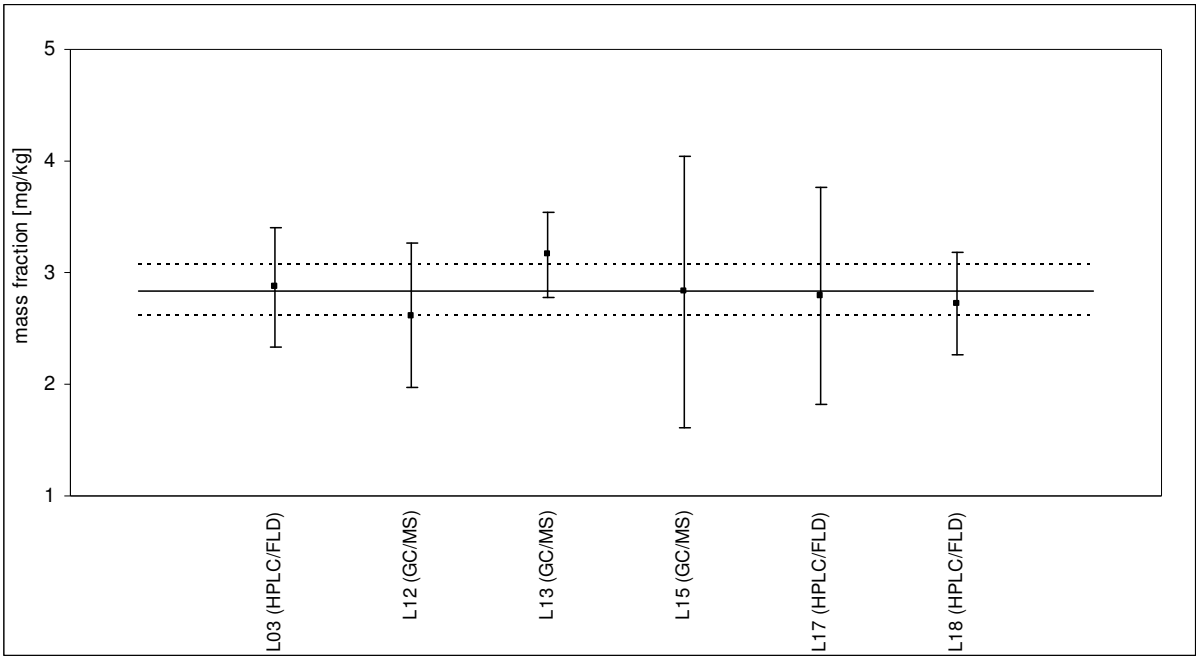
Lab-method code	Excluded results						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L01(GC/MS)	0.22	0.22	0.21	0.24	0.23	0.23	0.23	0.01	0.03
L02(GC/MS)	0.29	0.24	0.24	0.22	0.22	0.22	0.24	0.03	-
L04(HPLC/FLD)	0.12	0.13	0.11	0.12	0.12	0.11	0.12	0.01	0.02
L06(HPLC/FLD)	0.22	0.24	0.23	0.43	0.46	0.47	0.34	0.12	0.05
L10(GC/MS)	0.136	0.157	0.141	0.2	0.435	0.185	0.209	0.113	-
L11(GC/MS)	0.09	0.10	0.11	0.11	0.10	0.10	0.10	0.01	0.01
L14(GC/MS)	0.08	0.07	0.08	0.08	0.07	0.06	0.07	0.01	0.01
L16(HPLC/FLD)	0.197	0.243	0.288	0.242	0.176	0.228	0.229	0.039	0.11

Sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene

Lab-method code	Individual results[a]						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L03(GC/MS)	2.89	2.89	2.86	2.89	2.90	2.78	2.87	0.05	0.54
L12(GC/MS)	2.7	2.9	2.7	2.7	2.6	2.6	2.7	0.1	0.7
L13(GC/MS)	3.021	3.068	3.246	3.063	3.056	3.199	3.109	0.091	0.388
L15(GC/MS)	2.84	2.88	2.80	2.83	2.81	2.83	2.83	0.03	1.22
L17(HPLC/FLD)	3.061	3.031	2.975	3.178	2.983	2.826	3.009	0.116	0.977
L18(HPLC/FLD)	2.671	2.837	2.792	2.761	2.625	2.654	2.723	0.085	0.463

[a]: values reported on mass of the sample after conditioning the sample using conditions as described in EN12341

Error bars in the graph represent expanded uncertainties (U_{Lab}) as reported by the participating laboratories. Solid line represents the certified value. Broken lines represent the expanded uncertainty of the certified value.



Excluded results were not used for the calculation of the certified value.

Lab-method code	Excluded results						Mean value [mg/kg]	*s* [mg/kg]	U_{Lab} [mg/kg]
L01(GC/MS)	2.13	2.04	2.77	2.10	2.80	2.67	2.42	0.36	0.48
L04(HPLC/FLD)	3.1	3.25	3.11	3.05	3.25	3.21	3.16	0.09	0.47
L05(GC/MS)	1.93	2.03	2.12	2.00	2.03	1.70	1.97	0.15	0.22
L06(HPLC/FLD)	3.03	3.11	3.10	2.17	2.10	2.17	2.61	0.51	0.14
L10(GC/MS)	1.733	1.588	1.003	1.153	1.732	1.276	1.414	0.313	-
L11(GC/MS)	2.98	3.20	3.12	3.24	2.97	3.09	3.10	0.11	0.30
L14(GC/MS)	3.26	3.38	3.02	3.61	2.85	3.10	3.20	0.27	0.33
L16(HPLC/FLD)	1.818	1.809	1.742	1.79	1.58	1.522	1.710	0.127	0.271

Phenanthrene

Lab-method code	Result [mg/kg]						Mean value [mg/kg]	*s* [mg/kg]
L08(HPLC/FLD)	1.8	1.6	1.7	1.7	1.8	1.6	2.23	0.33
L11(GC/MS)	2.34	2.63	2.49	2.71	2.26	2.51		
L15(GC/MS)	2.42	2.46	2.39	2.33	2.25	2.50		
L18(HPLC/FLD)	2.356	2.328	2.302	2.349	2.321	2.315		

Anthracene

Lab-method code	Result [mg/kg]						Mean value [mg/kg]	*s* [mg/kg]
L08(HPLC/FLD)	0.21	0.19	0.20	0.20	0.21	0.18	0.28	0.07
L15(GC/MS)	0.36	0.37	0.37	0.38	0.37	0.38		
L18(HPLC/FLD)	0.253	0.248	0.255	0.251	0.284	0.274		

Fluoranthene

Lab-method code	Result [mg/kg]						Mean value [mg/kg]	*s* [mg/kg]
L08(HPLC/FLD)	4.62	4.30	4.56	4.50	4.80	4.40	4.67	0.58
L15(GC/MS)	5.65	5.33	5.45	5.54	5.21	5.16		
L18(HPLC/FLD)	4.050	4.360	3.970	4.190	4.000	3.960		

Pyrene

Lab-method code	Result [mg/kg]						Mean value [mg/kg]	*s* [mg/kg]
L08(HPLC/FLD)	4.70	4.43	4.64	4.65	4.90	4.60	4.59	0.81
L15(GC/MS)	5.89	5.46	5.28	5.45	5.48	5.48		
L18(HPLC/FLD)	3.60	3.49	3.42	3.78	3.81	3.56		

Chrysene

Lab-method code	Result [mg/kg]						Mean value [mg/kg]	*s* [mg/kg]
L08(HPLC/FLD)	1.71	1.64	1.75	1.71	1.80	1.70	1.61	0.29
L15(GC/MS)	1.83	1.87	1.92	1.86	1.84	1.89		
L18(HPLC/FLD)	1.19	1.14	1.34	1.12	1.35	1.31		

Benzo[*g,h,i*]pyrene

Lab-method code	Result [mg/kg]						Mean value [mg/kg]	*s* [mg/kg]
L08(HPLC/FLD)	2.02	1.90	2.03	2.15	2.2	2.10	1.76	0.31
L15(GC/MS)	1.95	1.81	1.81	1.86	1.79	1.81		
L18(HPLC/FLD)	1.35	1.35	1.28	1.48	1.39	1.43		

Coronene

Lab-method code	Result [mg/kg]						Mean value [mg/kg]	*s* [mg/kg]
L03(HPLC/FLD)	0.86	0.86	0.83	0.83	0.87	0.81	0.84	0.02

European Commission

EUR 24578 EN – Joint Research Centre – Institute for Reference Materials and Measurements
Title: The Certification of the Mass Fractions of selected Polycyclic Aromatic Hydrocarbons (PAHs) in fine dust (PM_{10}-like matrix), Certified Reference Material ERM®-CZ100
Author(s): M. Piaścik, E. Perez Przyk, A. Held
Luxembourg: Publications Office of the European Union
2010 – 50 pp. – 21.0 x 29.7 cm
EUR – Scientific and Technical Research series – ISSN 1018-5593
ISBN 978-92-79-17528-2
doi:10.2787/32299

Abstract

This report describes the preparation and certification of the new Reference Material (CRM) ERM-CZ100 PAHs in fine dust (PM_{10}-like).

Certification of the CRM included testing of the homogeneity and stability of the material as well as the characterisation using an intercomparison approach.

ERM-CZ100 was certified for its content of benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*j*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*c,d*]pyrene, dibenzo[*a,h*]anthracene and sum of benzo[*b*]fluoranthene, benzo[*k*]fluoranthene and benzo[*j*]fluoranthene.

The main purpose of the material is to assess method performance, i.e. for checking accuracy of analytical results in the field of air quality assurance. As any reference material, it can also be used for control charts or validation studies.

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LA- NA- 24578- EN- C

Publications Office

ISBN 978-92-79-17528-2