Institute for Reference Materials and Measurements

ERM European Reference Materials

CERTIFICATION REPORT

Certification of the Mass Fraction of Polycyclic Aromatic Hydrocarbons (PAHs) in Toluene

Certified Reference Materials ERM®-AC213

EUR 24644 EN – 2010

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Certification of the Mass Fraction of Polycyclic Aromatic Hydrocarbons (PAHs) in Toluene

Certified Reference Materials ERM®-AC213

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Certain commercial equipment, instruments, and materials are identified in this report to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the European Commission, nor does it imply that the material or equipment is necessarily the best available for the purpose.

Summary

This report describes the preparation of a calibration solution of polycyclic aromatic hydrocarbons (PAHs) (ERM-AC213) containing benzo[*a*]pyrene, benz[*a*]anthracene, cyclopenta[*cd*]pyrene, chrysene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, dibenz[*a*,*h*]anthracene, dibenzo[*a*,*l*]pyrene, dibenzo[*a*,*e*]pyrene, dibenzo[*a*,*i*]pyrene, indeno[1,2,3-*cd*]pyrene, 5-methylchrysene and benzo[*c*]fluorene and the certification of their content (mass fraction) in the solution.

The preparation of the calibrant, homogeneity and stability studies and confirmation measurements with a discussion of the results are described hereafter. Uncertainties were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [1] and include uncertainties due to the processing, purity assessment and possible instability.

The certified values are listed below:

Compound	Certified value [µg/g] [1)]	Uncertainty [µg/g] [2)]
Benzo[*a*]anthracene	3.09	0.04
Chrysene	3.06	0.05
5-methylchrysene	3.08	0.07
Benzo[*b*]fluoranthene	3.05	0.05
Benzo[*k*]fluoranthene	3.06	0.08
Benzo[*j*]fluoranthene	3.05	0.10
Benzo[*a*]pyrene	2.86	0.07
Indeno[1,2,3-*cd*]pyrene	3.04	0.05
Dibenz[*a*,*h*]anthracene	2.76	0.05
Benzo[*ghi*]perylene	3.07	0.05
Dibenzo[*a*,*l*]pyrene	2.85	0.10
Dibenzo[*a*,*e*]pyrene	2.97	0.10

[1)] The values are the mass fractions based on weighed amounts and purity. The values were confirmed experimentally by three laboratories.

[2)] The uncertainties are the expanded uncertainties ($k = 2$) of the values defined in [1)].

The indicative values are listed below:

Compound	Indicative value [µg/g] [1)]	Uncertainty [µg/g] [2)]
Benzo[*c*]fluorene	2.13	0.11
Cyclopenta[*cd*]pyrene	2.96	0.12
Dibenzo[*a,l*]pyrene	2.37	0.15

[1)] The values are the mass fractions based on weighed amounts and purity. The values were confirmed experimentally by three laboratories.

[2)] The uncertainties are the expanded uncertainties ($k = 2$) of the values defined in [1)].

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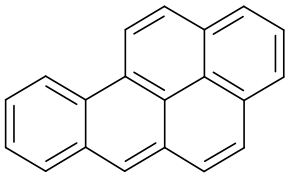
Glossary

Δ_m	Absolute difference between the mean measured value and the certified value
ANOVA	Analysis of variance
BCR	Community Bureau of Reference
BIPM	Bureau International des Poids et Mesures
C_m	Mean measured value
C_{CRM}	Certified value
CRM	Certified Reference Material
DSC	Differential scanning calorimeter
ERM®	European Reference Material
FAO	Food and Agriculture Organization of the United Nations
GC-FID	Gas chromatography with flame ionization detector
GCxGC	Comprehensive two dimensional gas chromatography
GC-IDMS	Gas chromatography with isotopic dilution mass spectrometry
GC-MS	Gas chromatography coupled to mass spectrometry
GUM	Guide to the Expression of Uncertainty in Measurement
HPLC-UV	High performance liquid chromatography with ultra violet detection
IRMM	Institute for Reference Materials and Measurements
JECFA	Joint FAO/WHO Expert Committee on Food Additives
JRC	Joint Research Centre
k	Coverage factor
MS_{among}	Mean square among ampoules from an ANOVA
MS_{within}	Mean square within an ampoule from an ANOVA
n	Number of replicates
OIML	International Organization of Legal Metrology
PAHs	Polycyclic Aromatic Hydrocarbons
RSD_{method}	Method repeatability expressed as relative standard deviation
s_{bb}	Between-unit variability expressed as a relative standard deviation
SCF	Scientific Committee on Food
SI	International Systems of Units
u	Standard uncertainty
u^*_{bb}	Relative uncertainty due to the inhomogeneity that can be hidden by the method repeatability
u_{CRM}	Combined uncertainty of certified value
U_{CRM}	Expanded combined uncertainty of certified value
$U_{CRM,rel}$	Expanded combined relative uncertainty of certified value
u_{lts}	Relative uncertainty of long-term stability
$u_{m,dil}$	Relative uncertainty for the mass of toluene in a stock solution
$u_{m,rel\ mix}$	Relative uncertainty for the mass of individual stock solutions
$u_{m,mix}$	Standard uncertainty for the mass of individual stock solutions
$u_{m,neat}$	Relative uncertainty for the mass of neat solids
$u_{m,rel\ sol}$	Combined relative uncertainty for the total mass of toluene
$u_{m,tol}$	Standard uncertainty for the mass of added toluene
u_{prep}	Relative uncertainty deriving from preparation
u_{pur}	Relative uncertainty of purity assessment
u_{sol}	Combined standard uncertainty for the total mass of toluene
u_Δ	combined uncertainty of the difference between the result and the certified value
$U_{\Delta.}$	expanded uncertainty of the difference between the result and the certified value
$\nu_{MSwithin}$	Degrees of freedom of MS_{within}
WHO	World Health Organization
$\bar{y}$	Average of all results of the homogeneity study

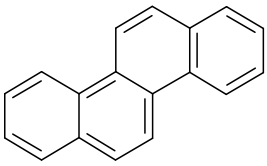
1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are widespread environmental pollutants which can be toxic and carcinogenic [2]. For non-smokers and non-occupational activities, air inhalation and food ingestion are the main routes of human exposure. In order to minimise the health risk from dietary PAHs exposure, a new Commission Regulation fixing maximum levels of benzo[*a*]pyrene in certain foodstuffs was adopted in February 2005 [3] following the recommendations of the Scientific Committee on Food (SCF) [4]. In addition, the SCF recommended a number of additional PAHs highlighted to be carcinogenic for which further investigation of the relative levels in certain foods was required (*i.e.* benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, chrysene, cyclopenta[*cd*]pyrene, dibenz[*a*,*h*]anthracene, dibenzo[*a*,*e*]pyrene, dibenzo[*a*,*h*]pyrene, dibenzo[*a*,*i*]pyrene, dibenzo[*a*,*l*]pyrene, indeno[1,2,3-*cd*]pyrene, 5-methylchrysene) [5]. In addition, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) recommended including benzo[*c*]fluorene as a further compound into future analyses as data on its occurrence in food are still scarce but indicate a possible carcinogenicity [6]. In Figure 1 the molecular structure of the target PAHs is shown.



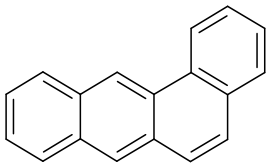
Benzo[*a*]pyrene

$C_{20}H_{12}$, MW = 252.3093 g/mol



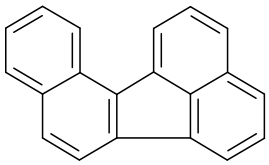
Chrysene

$C_{18}H_{12}$, MW = 228.2879 g/mol



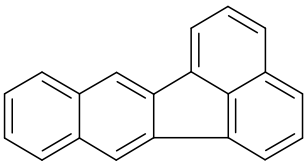
Benz[*a*]anthracene

$C_{18}H_{12}$, MW = 228.2879 g/mol



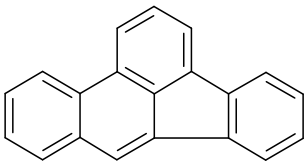
Benzo[*j*]fluoranthene

$C_{20}H_{12}$, MW = 252.3093 g/mol



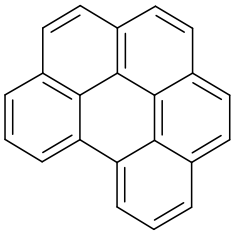
Benzo[*k*]fluoranthene

$C_{20}H_{12}$, MW = 252.3093 g/mol



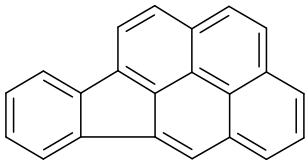
Benzo[*b*]fluoranthene

$C_{20}H_{12}$, MW = 252.3093 g/mol



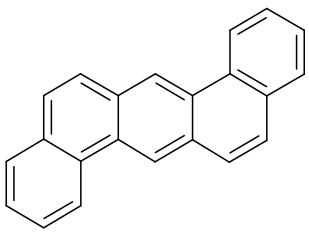
Benzo[*ghi*]perylene

$C_{22}H_{12}$, MW = 276.3307 g/mol



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

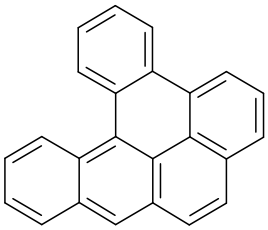
$C_{22}H_{12}$, MW = 276.3307 g/mol



Dibenz[*a*,*h*]anthracene

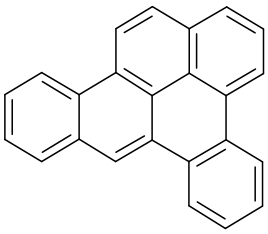
$C_{22}H_{14}$, MW = 278.3466 g/mol

Figure 1. Molecular structure of the PAHs present in ERM®-AC213.



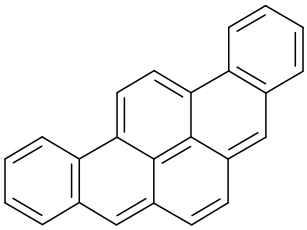
Dibenzo[*a,l*]pyrene

$C_{24}H_{14}$, MW = 302.3680 g/mol



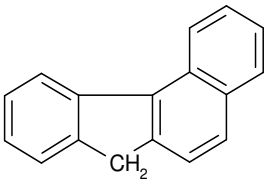
Dibenzo[*a,e*]pyrene

$C_{24}H_{14}$, MW = 302.3680 g/mol



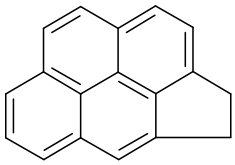
Dibenzo[*a,i*]pyrene

$C_{24}H_{14}$, MW = 302.3680 g/mol



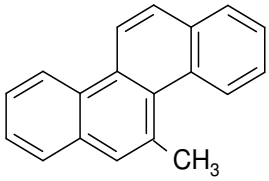
Benzo[*c*]fluorene

$C_{17}H_{12}$, MW = 216.2772 g/mol



Cyclopenta[*cd*]pyrene

$C_{18}H_{10}$, MW = 226.2720 g/mol



5-Methylchrysene

$C_{19}H_{14}$, MW = 242.3145 g/mol

Figure 1. *(cont.)* Molecular structure of the PAHs present in ERM®-AC213.

2. PARTICIPANTS

Project management, processing and data evaluation

- European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE

Purity determination

- European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Reference Materials Unit, Geel, BE
- Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, BE
- Bundesanstalt für Materialforschung und –prüfung (BAM), Berlin, DE

Homogeneity and stability studies

- European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, BE

Confirmation measurements

- European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), two independent laboratories, Geel, BE
- Vlaamse Instelling voor Technologisch Onderzoek (VITO), Mol, BE

3. PRODUCTION OF THE CALIBRATION SOLUTION

3.1. Purity assessment of the starting materials

The neat solids used to prepare the calibration solution were BCR or ERM certified reference materials except benzo[*c*]fluorene, cyclopenta[*cd*]pyrene and dibenzo[*a,i*]pyrene (Table 1). These last three compounds were purchased from different suppliers. Benzo[*c*]fluorene was purchased from Dr. Ehrenstorfer (Augsburg, Germany) with a stated purity of 0.982 g/g. Cyclopenta[*cd*]pyrene was purchased from the Biochemical Institute for Environmental Carcinogens (Grosshansdorf, Germany) with a declared purity of 0.996 g/g based on GC-FID. Dibenzo[*a,i*]pyrene was purchased from Campro Scientific (Veenendaal, The Netherlands) with a declared purity of 1.00 ± 0.04 g/g based on GC-MS.

Table 1. BCR®/ERM® certified reference materials and other neat solids used for the preparation of the calibration solution.

Compound	BCR® / ERM® code	Purity [g/g]	U [1)] [g/g]
Benzo[*c*]fluorene	[2)]	0.954	0.044
Benz[*a*]anthracene	BCR®-271	0.9984	0.0009
Cyclopenta[*cd*]pyrene	[2)]	0.973	0.031
Chrysene	BCR®-269	0.9928	0.0028
5-methylchrysene	BCR®-081R	0.9973	0.0013
Benzo[*b*]fluoranthene	BCR®-047	0.9974	0.0026
Benzo[*k*]fluoranthene	BCR®-048R	0.997	+ 0.003 - 0.004
Benzo[*j*]fluoranthene	BCR®-049	0.997	+ 0.003 - 0.006
Benzo[*a*]pyrene	ERM®-AC051	0.973	0.013
Indeno[1,2,3-*cd*]pyrene	ERM®-AC053	0.996	+ 0.004 - 0.005
Dibenz[*a,h*]anthracene	BCR®-138	0.990	0.007
Benzo[*ghi*]perylene	BCR®-052	0.9923	0.0021
Dibenzo[*a,l*]pyrene	BCR®-096	0.9972	0.0025
Dibenzo[*a,e*]pyrene	BCR®-133	0.996	+ 0.004 - 0.005
Dibenzo*[a,i]*pyrene	[2)]	0.955	0.052

[1)] The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor $k = 2$, corresponding to a level of confidence of about 95 %.

[2)] Commercial material, for purity estimation see Table 2.

A number of methods were used to further assess the purity of these three compounds such as DSC, HPLC-UV, GC-MS and GC-FID. Individual findings are summarized in Table 2.

Table 2. Purity of non-reference materials neat solids used for the preparation of the calibration solution and the standard deviation SD (n=3).

Compound	DSC [g/g] ± SD	HPLC-UV [g/g] ± SD	GC-MS [g/g] ± SD	GC-FID [g/g] ± SD [1)]	Established purity [g/g] ± U
Benzo[c]fluorene	0.991 ± 0.003	0.916 ± 0.009	0.991 ± 0.001	0.980 ± 0.002	0.954 ± 0.044
Cyclopenta[cd]pyrene	1.000 ± 0.001	0.953 ± 0.004	0.984 ± 0.002	0.943 ± 0.004	0.973 ± 0.031
Dibenzo[a,i]pyrene	0.979 ± 0.005	0.910 ± 0.011	0.999 ± 0.001	0.979 ± 0.002	0.955 ± 0.052

[1)] n=6

The purity of the toluene was assessed by GC-FID, GC-MS and HPLC-UV. No relevant impurities were detected. The associated uncertainty is assumed to be negligible and was therefore not considered in any uncertainty budgets.

3.2. Preparation and filling of the calibration solution

Individual stock solutions of the target PAHs were prepared gravimetrically in toluene. The weighing procedure took place in a controlled stable environment (temperature 20 ± 2°C, relative humidity 50 ± 20 %). To minimize influence from static electricity an anti-static fan (Sartorious Y1B01) was used on the occasions when there was no risk of disseminating powdery substances. The neat solids were weighed in weighing boats using the double-substitution weighing procedure, in which a standard and an unknown weight are intercompared twice to determine the average difference between the two weights. In this way, calibration bias of the balance is eliminated since the balance is used just as a comparator (OIML international recommendation R111 [7]). When substitution weighing is performed, traceability to SI is directly realised by the mass standards, thus lowering the uncertainty of the measurement result. The linearity component in the balance uncertainty is negligible since the mass difference between mass standards and sample was sufficiently low. Dibenzo[*a*,*h*]pyrene is present in the calibration solution, however no value has been assigned.
Once the amounts of neat solid were weighed, they were transferred with the weighing boat into glass vials. In a second step the solvent (toluene was added gravimetrically to each glass vial.
The final calibration solution containing all the target compounds was prepared by mixing fixed amounts of each individual stock solution and further gravimetric addition of toluene to reach the desired final mass fraction

The masses and their uncertainties for each compound and for the final calibration solution are summarized in Table 3 and Table 4. The uncertainties of these gravimetrical preparations are obtained

by taking into account the uncertainty of each weighing step (see formulas below). This resulted in uncertainties of u_{prep} between 0.11 % and 0.18 %.

2 mL of the calibration solution were filled in 5 mL amber glass ampoules flushed with argon. The ampoules were flame sealed and checked for leaks. Approximately 1900 ampoules were filled.

Table 3. Gravimetric preparation of the individual stock solutions and the assigned relative uncertainty.

Compound	Mass [g]	$u_{m,\ neat}$ [%] [1)]	Mass toluene [g]	$u_{m,\ dil}$ [%] [1)]
Benzo[*c*]fluorene	0.00864	0.174	87.23842	0.00010
Benz[*a*]anthracene	0.01406	0.107	103.06253	0.00009
Cyclopenta[*cd*]pyrene	0.01233	0.122	105.03471	0.00009
Chrysene	0.01259	0.119	103.24832	0.00009
5-methylchrysene	0.01238	0.121	103.96791	0.00009
Benzo[*b*]fluoranthene	0.01345	0.112	102.33362	0.00009
Benzo[*k*]fluoranthene	0.01162	0.129	103.06670	0.00009
Benzo[*j*]fluoranthene	0.01224	0.123	103.49615	0.00009
Benzo[*a*]pyrene	0.01111	0.135	103.16402	0.00009
Indeno[1,2,3-*cd*]pyrene	0.01157	0.130	103.17288	0.00009
Dibenz[*a,h*]anthracene	0.01056	0.142	103.29193	0.00009
Benzo[*ghi*]perylene	0.01239	0.121	102.47393	0.00009
Dibenzo[*a,l*]pyrene	0.01069	0.140	101.81139	0.00009
Dibenzo[*a,e*]pyrene	0.01121	0.134	102.80238	0.00009
Dibenzo[*a,i*]pyrene	0.00941	0.159	103.63398	0.00009

[1)] Relative expanded uncertainty estimated in accordance with the ISO/BIPM Guide to the expression of Uncertainty in Measurements with a coverage factor $k = 2$, corresponding to a level of confidence of about 95%.

Table 4. Gravimetric preparation of the mixed solution from the individual stock solutions.

Compound	Mass [g]	$u_{m,\,mix}$ [g]	Mass toluene [g]	$u_{m,\,tol}$ [g]	u_{sol} [g]	u_{prep} [%]
Benzo[*c*]fluorene	83.10	0.01	2151.15	0.02	0.06	0.18
Benz[*a*]anthracene	83.56	0.01				0.11
Cyclopenta[*cd*]pyrene	95.46	0.01				0.12
Chrysene	92.98	0.01				0.12
5-methylchrysene	95.26	0.01				0.12
Benzo[*b*]fluoranthene	85.49	0.01				0.11
Benzo[*k*]fluoranthene	100.09	0.01				0.13
Benzo[*j*]fluoranthene	95.15	0.01				0.12
Benzo[*a*]pyrene	100.27	0.01				0.14
Indeno[1,2,3-*cd*]pyrene	100.17	0.01				0.13
Dibenz[*a*,*h*]anthracene	100.22	0.01				0.14
Benzo[*ghi*]perylene	94.25	0.01				0.12
Dibenzo[*a*,*l*]pyrene	100.17	0.01				0.14
Dibenzo[*a*,*e*]pyrene	100.42	0.01				0.14
Dibenzo[*a*,*i*]pyrene	100.60	0.01				0.16

The standard uncertainty of the total mass of toluene was calculated as:

$$u_{sol} = \sqrt{\sum u_{m,mix}^2 + u_{m,tol}^2}$$

u_{sol} combined standard uncertainty for the total mass of toluene
$u_{m,mix}$ standard uncertainty for the mass of individual stock solutions
$u_{m,tol}$ standard uncertainty for the mass of added toluene

The relative uncertainty from the preparation (u_{prep}) was calculated for each compound combining the relative uncertainty from each individual weighing step and the combined relative uncertainty for the weighing of toluene.

$$u_{prep} = \sqrt{\left(u_{m,neat}\right)^2 + \left(u_{m,dil}\right)^2 + \left(u_{m,rel,mix}\right)^2 + \left(u_{rel,sol}\right)^2}$$

$u_{m,neat}$ relative uncertainty for the mass of neat solids
$u_{m,dil}$ relative uncertainty for the mass of toluene in stock solutions
$u_{rel,sol}$ combined relative uncertainty for the total mass of toluene
$u_{m,rel,mix}$ relative uncertainty for the mass of individual stock solutions

3.3. Homogeneity studies

For the homogeneity study, 13 samples were chosen using a random stratified sample picking scheme. Three independent replicates of each sample were measured by GC-IDMS in a random order in one analytical run, i.e. under repeatability conditions, to allow distinction between an analytical trend and a trend in the filling sequence. Results are given in ANNEX A and were evaluated to detect trends regarding filling or analysis sequence and to estimate the uncertainty contribution from possible heterogeneity.

The distribution of ampoule averages was checked employing normal probability plots for normal distribution and histograms for unimodal distribution. The data were also tested for outliers using the single and double Grubbs test. Further the data were tested for a trend in ampoule averages, which would indicate a filling trend during ampouling. Results were then evaluated by a one-way analysis of variance (ANOVA) and the following figures were calculated:

- Method repeatability (RSD_{method}) expressed as a relative standard deviation:

$$RSD_{method} = \frac{\sqrt{MS_{within}}}{\bar{y}}$$

MS_{within} mean square within an ampoule from an ANOVA

$\bar{y}$ average of all results of the homogeneity study

- Between-unit variability (s_{bb}) expressed as a relative standard deviation:

$$s_{bb} = \frac{\sqrt{\frac{MS_{among} - MS_{within}}{n}}}{\bar{y}}$$

MS_{among} mean square among ampoules from an ANOVA

n number of replicates per ampoules

- The heterogeneity that can be hidden by method repeatability, expressed as relative uncertainty, which is used as the minimum uncertainty contribution from homogeneity:

$$u_{bb}^{*} = \frac{RSD_{method}}{\sqrt{n}} \sqrt[4]{\frac{2}{\nu_{MSwithin}}}$$

$\nu_{MSwithin}$ degrees of freedom of MS_{within}

Conclusions:

No significant trends regarding the filling sequence were detected. Ampoule averages followed a unimodal distribution. Some outliers were detected at a 95 % level of confidence using the Grubbs test. However, they were not excluded since no technical reason was found to do so. In Table 5 the calculated maximum possible heterogeneity is shown as u^*_{bb}.

Table 5. Maximum possible heterogeneity (u^*_{bb}) obtained for ERM®-AC213.

Compound	u^*_{bb} [%]
Benzo[*c*]fluorene	0.55
Benz[*a*]anthracene	0.20
Cyclopenta[*cd*]pyrene	0.52
Chrysene	0.49
5-methylchrysene	0.60
Benzo[*b*]fluoranthene	0.36
Benzo[*k*]fluoranthene	0.37
Benzo[*j*]fluoranthene	0.43
Benzo[*a*]pyrene	0.49
Indeno[1,2,3-*cd*]pyrene	0.29
Dibenz[*a,h*]anthracene	0.27
Benzo[*ghi*]perylene	0.43
Dibenzo[*a,l*]pyrene	0.76
Dibenzo[*a,e*]pyrene	0.69
Dibenzo[*a,i*]pyrene	0.71

PAHs in toluene can be expected to be a homogeneous solution, and at the mass fraction level in the material and the typical sample intake can be expected to have a negligible heterogeneity. Nevertheless, the homogeneity study is used to check for any possible heterogeneity due to contamination, evaporation or any other effect occurring during the production process.

The minimum sample intake is 0.3 g. The homogeneity and stability studies were performed using 0.3 g of calibration solution, proving that the individual samples are homogeneous at least to this level.

3.4. Stability studies

Two stability studies were performed, one 4 weeks isochronous study (short-term stability study) to evaluate the stability of the materials during transport and one 18 months isochronous study (long-term stability study) to evaluate stability during storage.

3.4.1. Short-term stability study

For this study, samples were stored in the dark at 4 °C, 18 °C and 60 °C as well as at the reference temperature (-20 °C). Two ampoules were stored at each temperature for 0, 1, 2 and 4 weeks (June 2007 - July 2007). After the indicated periods the samples were transferred to the reference temperature until analysis. After completion of the scheme, two independent replicates of each sample were measured under repeatability conditions by GC-IDMS. The data obtained are given in ANNEX B and were plotted against storage time at a given test temperature. The regression line was tested for significant trends (degradation, enrichment) which might occur due to storage conditions. The regression line was calculated and the slope tested for statistical significance at 95 % and 99 % level of confidence.

Conclusions short-term stability study:

Some outliers were detected at the temperatures studied using the Grubbs outlier test. However, these outliers were not excluded since after scrutinising the data no technical reason was found to do so. No significant trends regarding the analytical sequence were detected. No significant slope at 95 % level of confidence was detected except for chrysene at 4 °C and benzo[*b*]fluoranthene at 18 °C. At 60 °C the slope was significant at 95 and 99 % level of confidence for cyclopenta[*cd*]pyrene and benzo[*ghi*]perylene.

3.4.2. Long-term stability study

For this study, samples were stored at 4 °C and 18 °C, as well as at the reference temperature (- 20 °C). Three ampoules were stored at each temperature for 0, 6, 12 and 18 months (June 2007 - December 2008). After completion of the storage scheme, two independent replicates of each ampoule were measured under repeatability conditions by GC-IDMS. Results are given in ANNEX C and were checked for significant trends depending on storage conditions and time. The resulting slopes were tested for their significance at 95 % and 99 % level of confidence.

Conclusions long-term stability study (18 months):

Some outliers were found in the data obtained. As there was no technical reason to exclude them from evaluation, they remained in the data set. No significant trends regarding the analytical sequence were detected. The data points were plotted against time and the regression line calculated. For all compounds the slope of the regression line at 4 °C was found to be insignificant at a 95 and 99 % confidence level. At 18 °C, the slope of the regression line was significant for cyclopenta[*cd*]pyrene and chrysene. For this reason it was decided to store the ERM-AC213 at -20 °C.

The uncertainty due to possible degradation (u_{lts}) was calculated for a storage time of 18 months at 4 °C as follows:

$$u_{lts,rel} = \frac{RSD_{stab}}{\sqrt{\sum (t_i - \bar{t})^2}} \cdot t$$

With RSD_{stab} being the relative standard deviation of all results of the stability study, t_i being the time point for each replicate, $\bar{t}$ being the average of all time points and t being the pre-defined shelf life (24 months at 4 °C in this case). The results are summarised in Table 6.

Table 6. Uncertainty contribution due to storage 18 months (u_{lts}, %) obtained for ERM®-AC213.

Compound	u_{lts} [%]
Benzo[*c*]fluorene	1.00
Benz[*a*]anthracene	0.60
Cyclopenta[*cd*]pyrene	1.00
Chrysene	0.60
5-methylchrysene	0.90
Benzo[*b*]fluoranthene	0.60
Benzo[*k*]fluoranthene	1.20
Benzo[*j*]fluoranthene	1.40
Benzo[*a*]pyrene	0.80
Indeno[1,2,3-*cd*]pyrene	0.60
Dibenz[*a,h*]anthracene	0.60
Benzo[*g,h,*i]perylene	0.60
Dibenzo[*a,l*]pyrene	1.50
Dibenzo[*a,e*]pyrene	1.40
Dibenzo[*a,i*]pyrene	1.30

3.4.3. General conclusions for the stability studies

No significant slope at 95 % level of confidence was detected in the short term stability study for the compounds present in the calibration solution at 4 °C, except for chrysene. In the long-term stability study (4 °C, 18 months) the same compound showed no significant slope of the regression line at 95 % level of confidence, indicating its stability at this temperature. Stability of chrysene and cyclopenta[*cd*]pyrene were not consistent in the long-term stability study at 18 °C (18 months), where these two compounds showed significant slope at 95% level of confidence. Although the calibration solution is stable in both short-term and long-term stability (18 months) studies at 4 °C it was decided for safety reasons to move the calibration solution to a storage temperature of -20 °C. For the shipment cooling elements should be used to prevent possible degradation of the material.

The material will be subjected to IRMM's regular stability monitoring programme to ensure stability beyond the initial shelf-life.

4. CHARACTERIZATION

The mass fraction of the target PAHs in the calibration solution is certified on the basis of the gravimetric preparation and the estimated purity of the crystalline substances. The mass fractions were verified by GC-MS analysis to exclude losses or introduction of artefacts during the preparation and ampouling steps.

Three laboratories measured 3 ampoules of the calibration solution by GC-IDMS at least in duplicate. Lab 1 measured on one day, whereas Lab 2 measured on different days and different chromatographic conditions. Lab 3 is not reported due to lack of repeatability although its results were overlapping with the certified values. In ANNEX D is presented the values obtained by the laboratories which were not significantly different to the mass fraction in the CRM as determined gravimetrically. No values are given for benzo[b]fluoranthene and benzo[j]fluoranthene from Lab 2 using column DB-5MS as the compounds are not separated on this column. Consequently the certified mass fraction was confirmed.

On the basis of the gravimetric preparation the combined uncertainty of the certified value (u_{CRM}) includes contributions from purity assessment (u_{pur}), gravimetric preparation (u_{prep}), long-term stability (u_{lts}) and inhomogeneity between units (u_{bb}). Contributions of shipment to the overall uncertainty were found to be negligible and are therefore not included in the uncertainty budget, as well as the contribution of the between-unit heterogeneity. This combined uncertainty (u_{CRM}) is calculated as the square root of the sum of the squares of each contribution. u_{CRM} was multiplied with a coverage factor of two ($k = 2$) to express the expanded uncertainty (U_{CRM}). U_{CRM} corresponds to a confidence interval of approximately 95 %. Certified values and contributions to the uncertainty budget are summarized in Table 7.

Table 7. Certified values and uncertainties for AC213.

Compounds in ERM-AC213	Certified mass fraction [µg/g]	u_{prep} [%]	u_{pur} [%]	u_{bb} [%]	u_{lts} [%]	u_{CRM} [%]	$U_{CRM,rel}$ [%]	U_{CRM} [µg/g]
Benz[*a*]anthracene	3.09	0.11	0.05	0.20	0.60	0.64	1.29	0.04
Chrysene	3.06	0.12	0.14	0.49	0.60	0.80	1.59	0.05
5-methylchrysene	3.08	0.12	0.07	0.60	0.90	1.09	2.18	0.07
Benzo[*b*]fluoranthene	3.05	0.11	0.13	0.36	0.60	0.72	1.44	0.05
Benzo[*k*]fluoranthene	3.06	0.13	0.20	0.37	1.20	1.28	2.56	0.08
Benzo[*j*]fluoranthene	3.05	0.12	0.30	0.43	1.40	1.50	3.00	0.10
Benzo[*a*]pyrene	2.86	0.14	0.67	0.49	0.80	1.16	2.32	0.07
Indeno[1,2,3-*cd*]pyrene	3.04	0.13	0.22	0.29	0.60	0.72	1.43	0.05
Dibenz[*a*,*h*]anthracene	2.76	0.14	0.36	0.27	0.60	0.76	1.52	0.05
Benzo[*ghi*]perylene	3.07	0.12	0.11	0.43	0.60	0.76	1.51	0.05
Dibenzo[*a*,*l*]pyrene	2.85	0.14	0.13	0.76	1.50	1.69	3.39	0.10
Dibenzo[*a*,*e*]pyrene	2.97	0.14	0.25	0.69	1.40	1.59	3.17	0.10

Due to the relatively large uncertainty of the purity of other PAHs, the following indicative values have been assigned for them in ERM AC213:

Table 8. Indicative values and their uncertainties for ERM AC213.

Compounds in ERM-AC213	Indicative mass fraction [µg/g]	u_{prep} [%]	u_{pur} [%]	u_{bb} [%]	u_{lts} [%]	u_{CRM} [%]	$U_{CRM,rel}$ [%]	U_{CRM} [µg/g]
Benzo[*c*]fluorene	2.13	0.18	2.26	0.55	1.00	2.54	5.08	0.11
Cyclopenta[*cd*]pyrene	2.96	0.12	1.58	0.52	1.00	1.95	3.90	0.12
Dibenzo[*a*,*i*]pyrene	2.37	0.16	2.69	0.71	1.30	3.08	6.15	0.15

5. METROLOGICAL TRACEABILITY

The identities of the PAHs present in the solution have been confirmed by mass spectrometry determination. Their identities are confirmed beyond reasonable doubt.

All dilutions were performed gravimetrically on balances with calibrated weights. The gravimetric values traceable to the SI were confirmed by GC-IDMS measurements.

6. INSTRUCTIONS FOR USE

6.1. Storage conditions

The material should be stored at or below -20 ± 5 ºC until use. However, the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of open samples.

6.2. Safety precautions

The main hazard in this formulation derives from the solvent, toluene. For this the following Hazard (H) and Precautionary (P) statements apply:

H225	Highly flammable liquid and vapour
H304	May be fatal if swallowed and enters airways
H361	Suspected of damaging fertility or the unborn child
H373	May cause damage to organs through prolonged or repeated exposure
H315	Causes skin irritation
H336	May cause drowsiness or dizziness
P210	Keep away from heat/sparks/open flames/hot surfaces. – No smoking
P301/P310	IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician.
P331	Do NOT induce vomiting
P302/P352	IF ON SKIN: Wash with plenty of soap and water

6.3. Use of the certified value

The main purpose of this material is for instrument calibration (e.g. external calibration, standard addition), method validation and QC purposes This material can also be used to assess the trueness of the value of own calibration solutions. In this case, the measured values of the CRMs are compared with the certified values with the following procedure:

• Calculate the absolute difference (Δ_m) between the mean measured value (c_m) and the certified value (c_{CRM})

$$\Delta_m = \left| c_m - c_{CRM} \right|$$

• Calculate the uncertainty of Δ_m (u_Δ) by combining the measurement uncertainty (u_m) with the uncertainty of the certified value (u_{CRM}) as follows:

$$u_\Delta = \sqrt{u_m^2 + u_{CRM}^2}$$

• 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 %.

A more detailed explanation on the procedure can be found in: ERM application note 1 (www.erm-CRM.org), or in www.irmm.jrc.be/html/reference_materials_catalogue/user_support/use.htm

7. ACKNOWLEDGMENTS

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8. REFERENCES

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[2] K. Straif, R, Baan, Y. Grosse, B. Secretan, F. El Ghissassi, V. Cogliano, on behalf of the WHO International Agency for Research on Cancer Monograph Working Group, Lancet Oncol. 6 (2005) 931.

[3] Commission Regulation (EC) No 208/2005 of 4 February 2005 amending Regulation (EC) No 466/2001 as regards polycyclic aromatic hydrocarbons. OJEU 2005, L34/3-5.

[4] Opinion of the Scientific Committee on Food on the risks to human health of Polycyclic Aromatic Hydrocarbons in food (expressed on 4 December 2002). Joint FAO/WHO Expert Committee on Food Additives. Available at: http://ec.europa.eu/food/fs/sc/scf/index_en.html

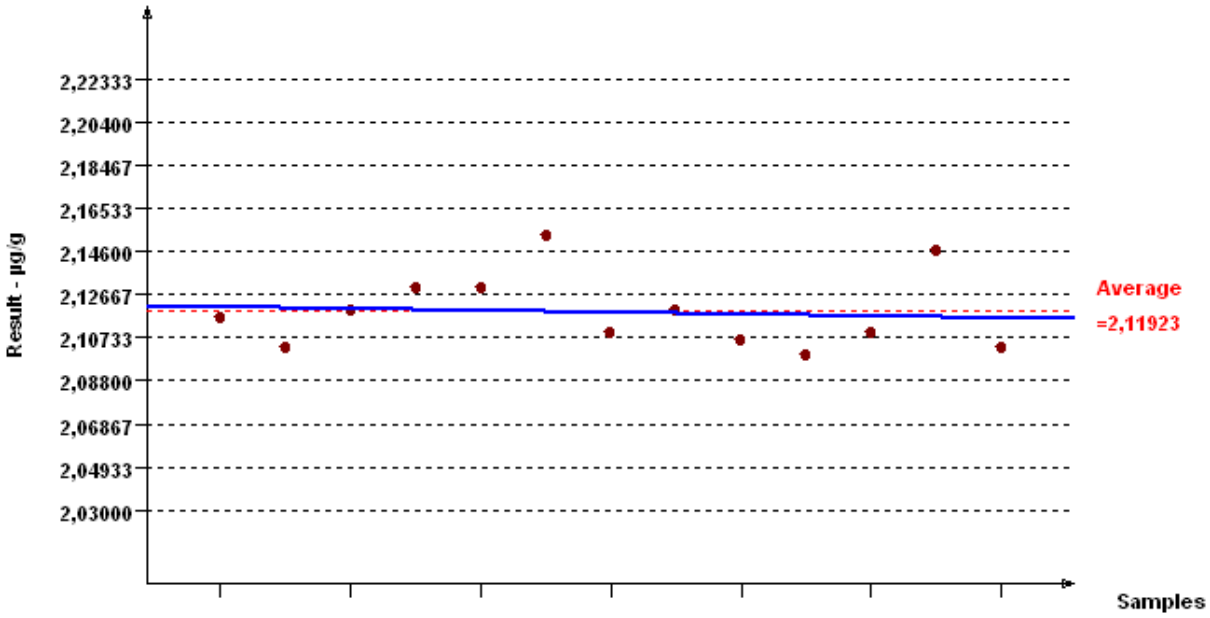
[5] Commission Recommendation of 4 February 2005 on the further investigation into the levels of polycyclic aromatic hydrocarbons in certain foods. OJEU 2005, L34/43-45.

[6] Joint FAO/WHO Expert Committee on Food Additives. Sixty-fourth meeting, Rome, 8-17 February 2005. Available at: http://www.who.int/ipcs/food/jecfa/summaries/en/

[7] OIML R111 "Weights of Classes E_1, E_2, F_1, F_2, M_1, M_{1-2}, M_2, M_{2-3} and $M_{3.}$ http://www.oiml.org

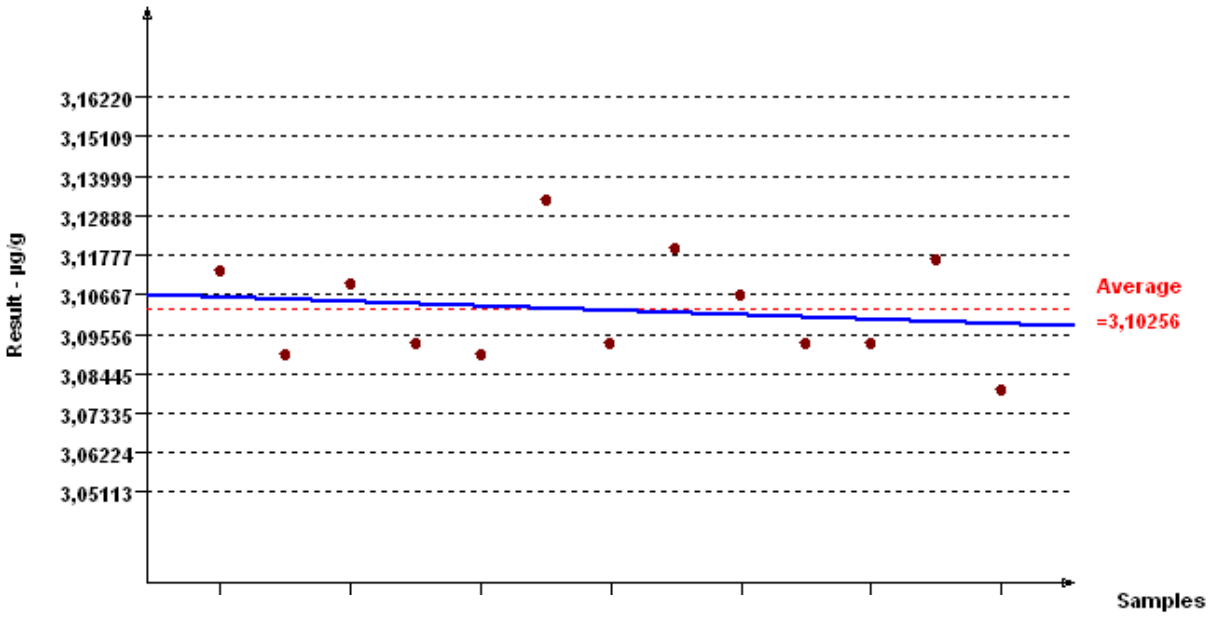
ANNEX A. Homogeneity data

Benzo[*c*]fluorene – Graph sample means



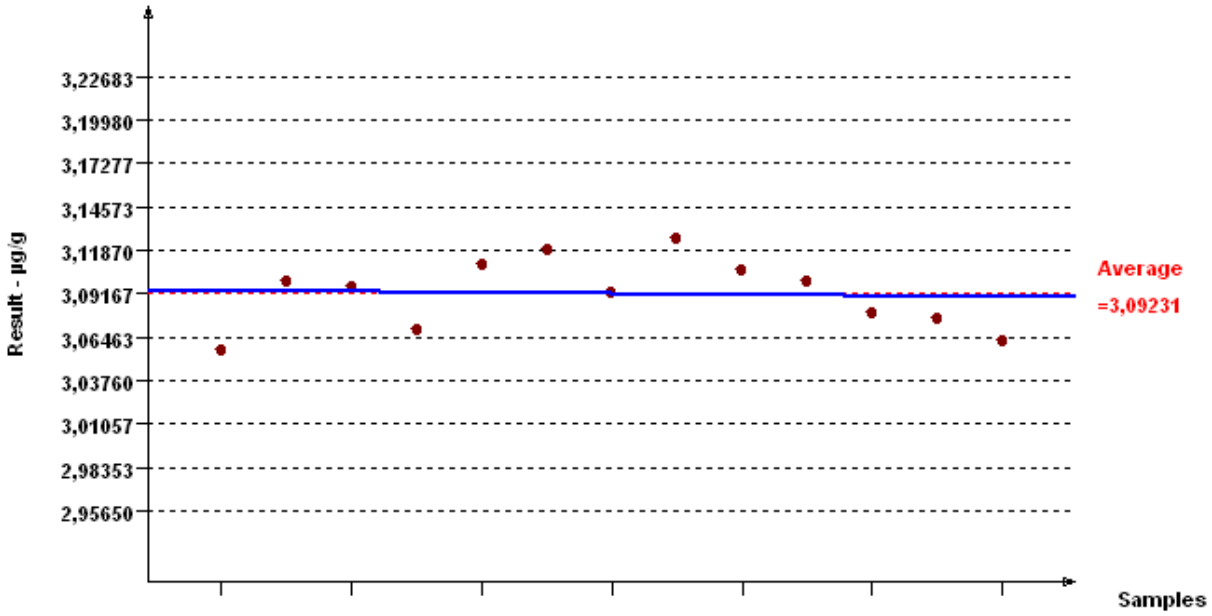
The tested samples cover the whole production range

Benzo[*a*]anthracene – Graph sample means



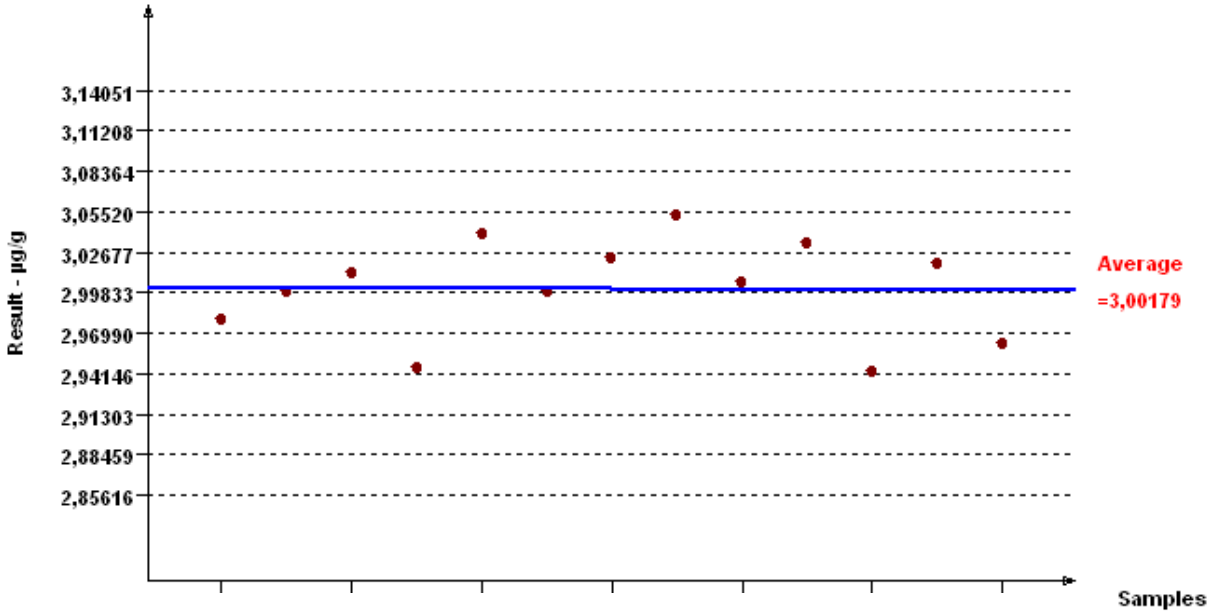
The tested samples cover the whole production range

Chrysene – Graph sample means



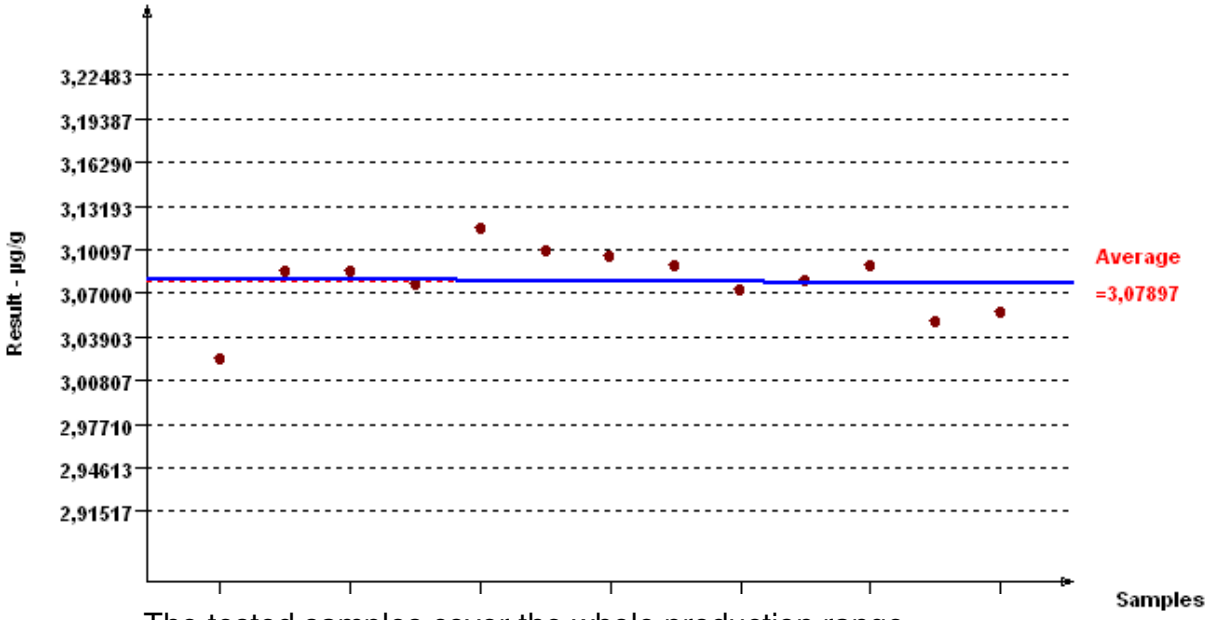
The tested samples cover the whole production range

Cyclopenta[*cd*]pyrene– Graph sample means



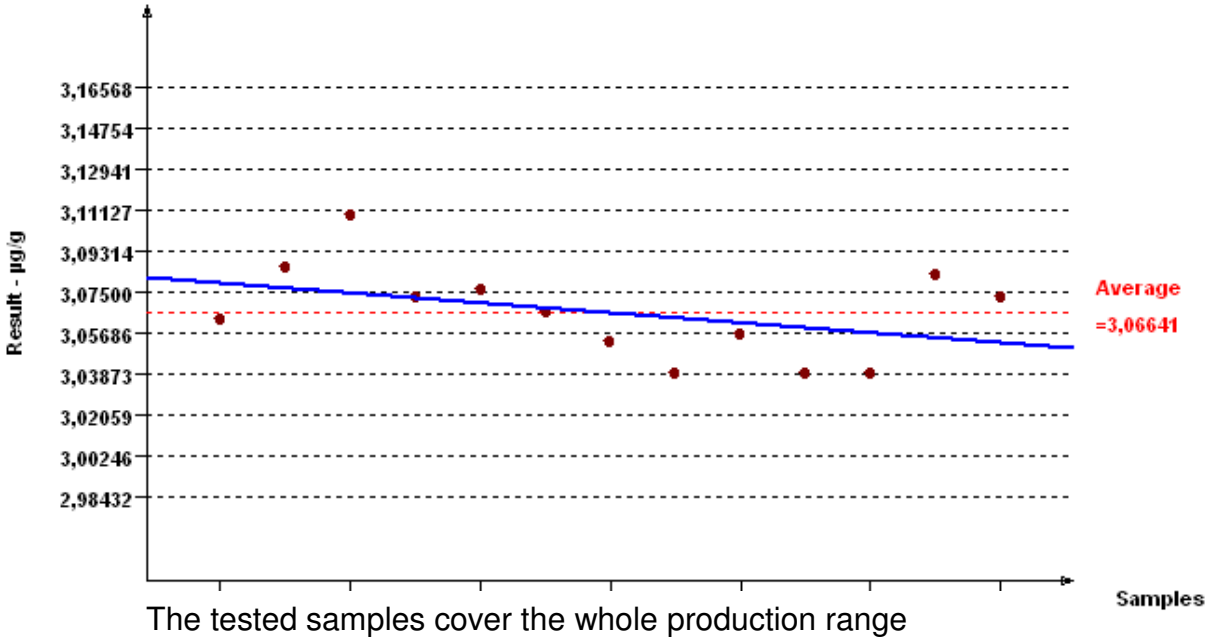
The tested samples cover the whole production range

5-Methylchrysene – Graph sample means



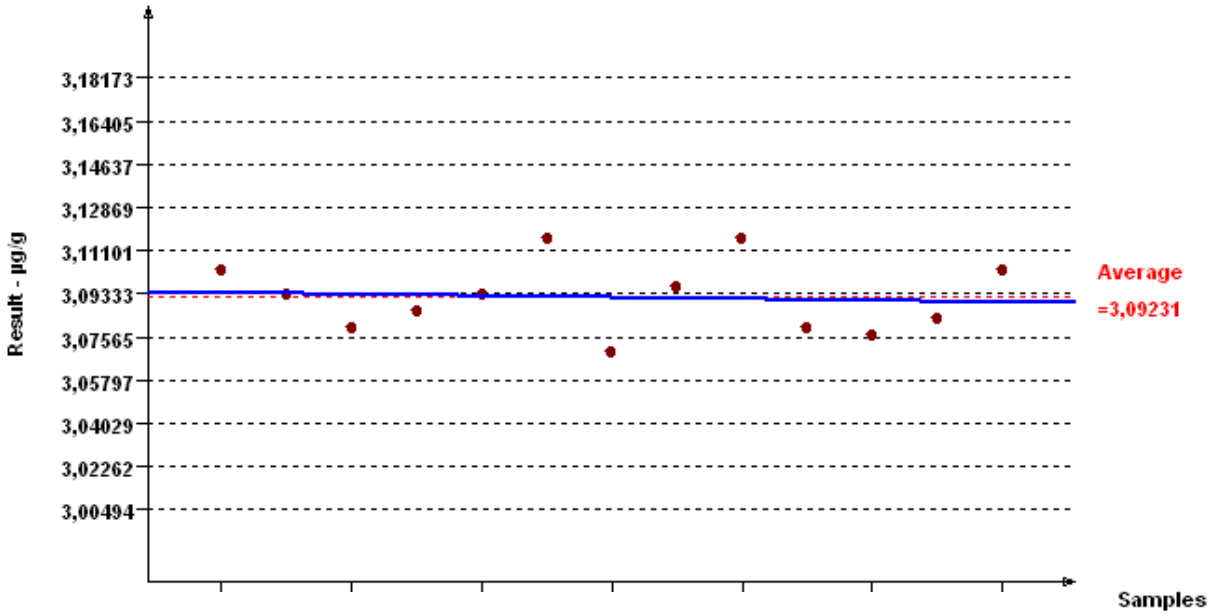
The tested samples cover the whole production range

Benzo[*b*]fluoranthene – Graph sample means



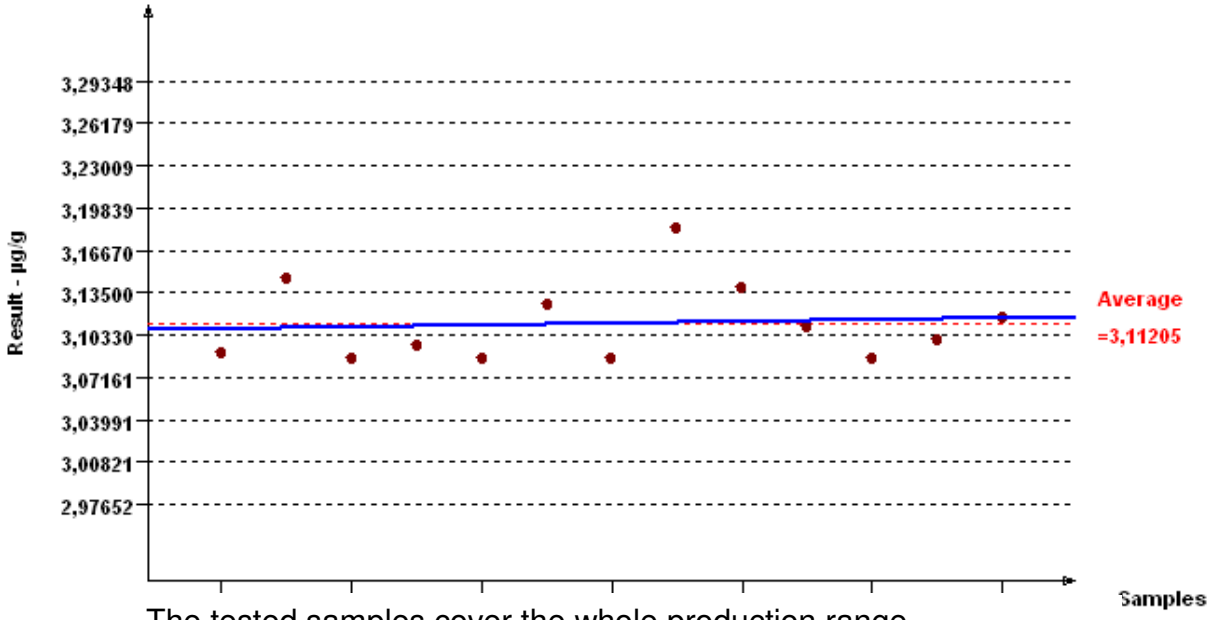
The tested samples cover the whole production range

Benzo[*k*]fluoranthene – Graph sample means



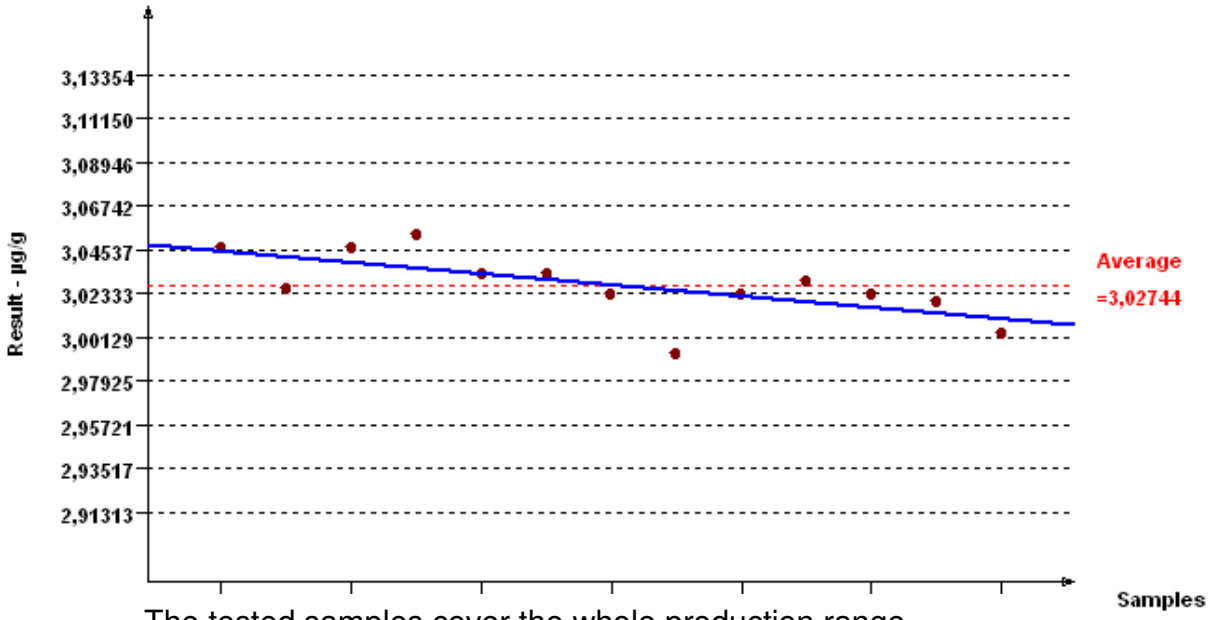
The tested samples cover the whole production range

Benzo[*j*]fluoranthene – Graph sample means



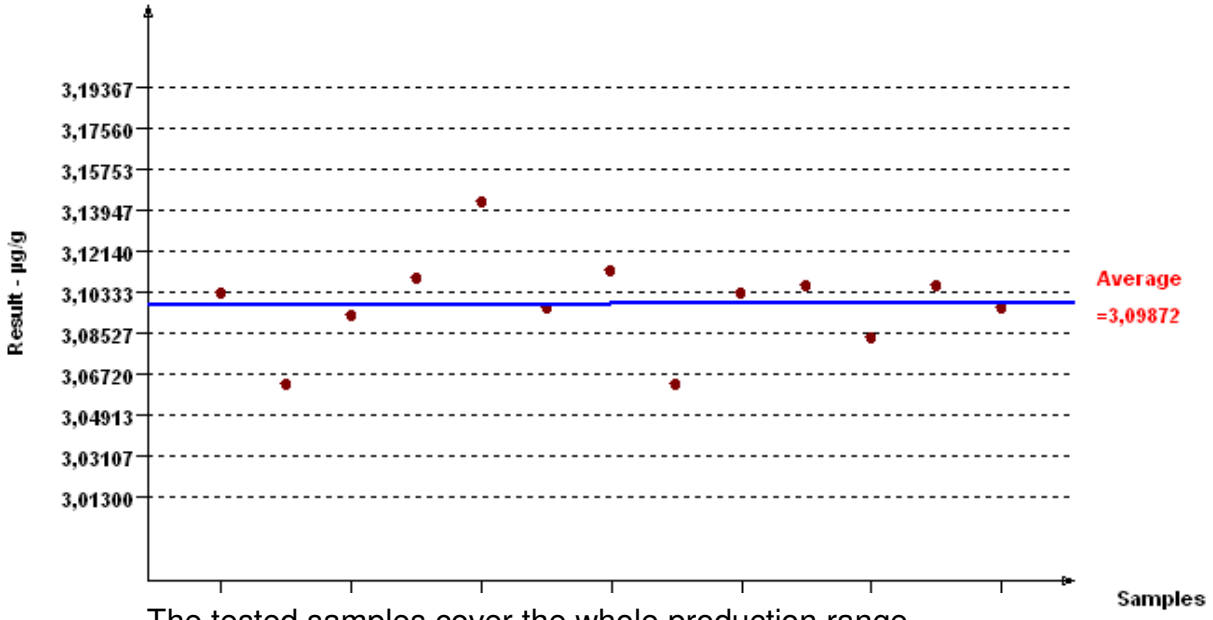
The tested samples cover the whole production range

Benzo[*a*]pyrene – Graph sample means



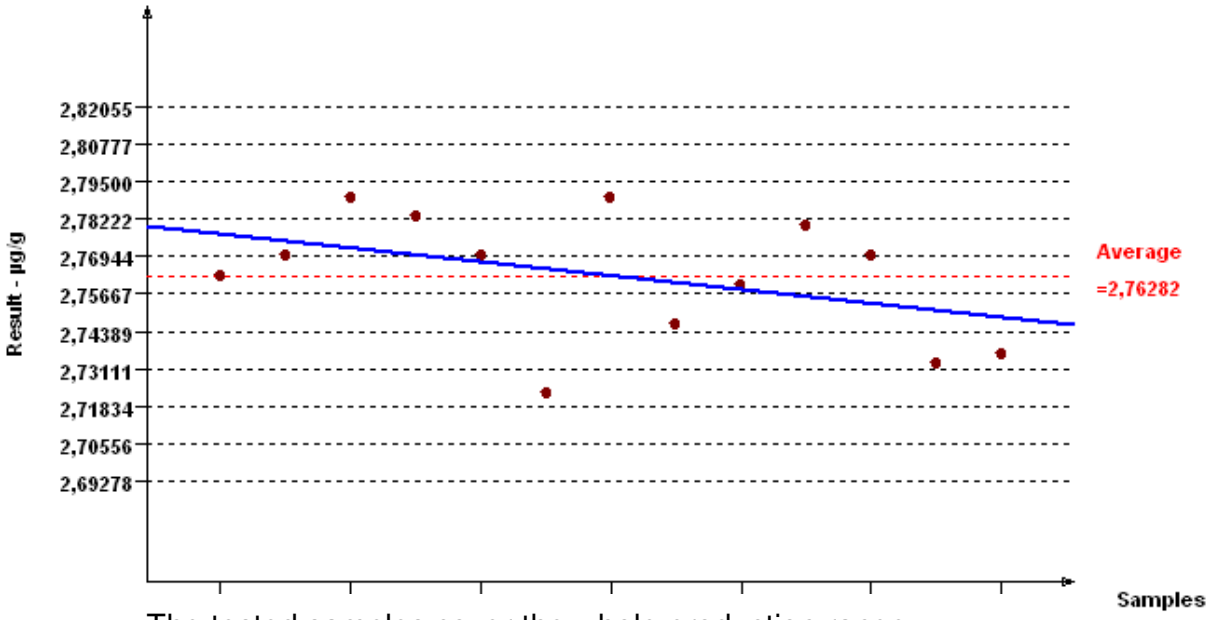
The tested samples cover the whole production range

Indeno[1,2,3-*cd*]pyrene – Graph sample means



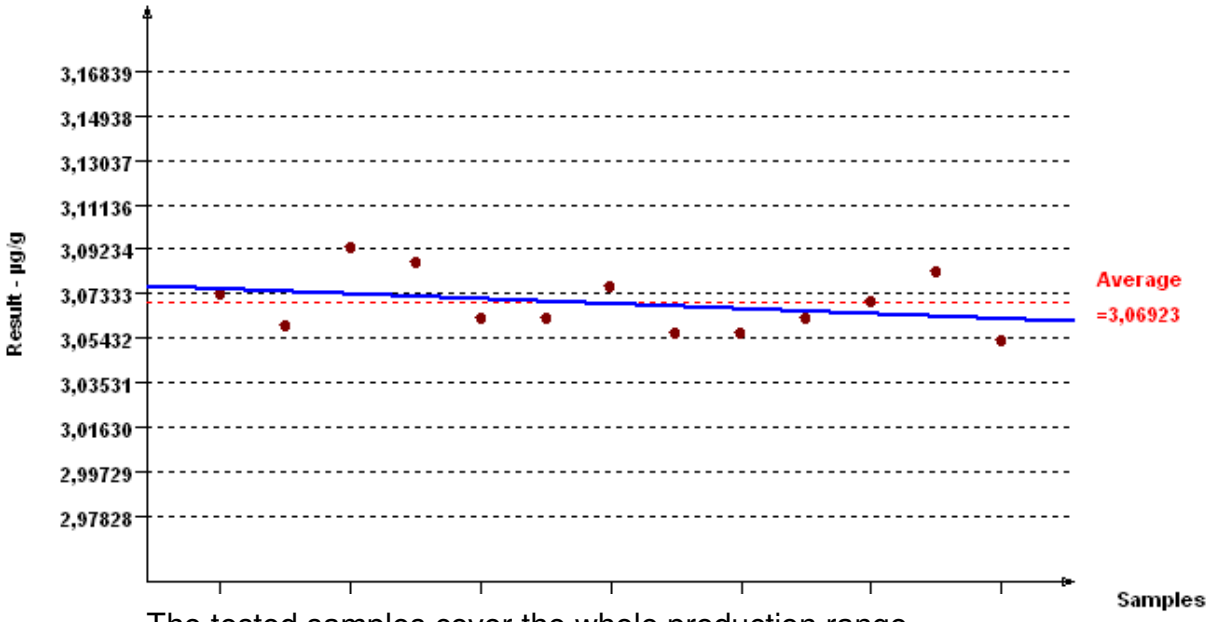
The tested samples cover the whole production range

Dibenz[*a,h*]anthracene – Graph sample means



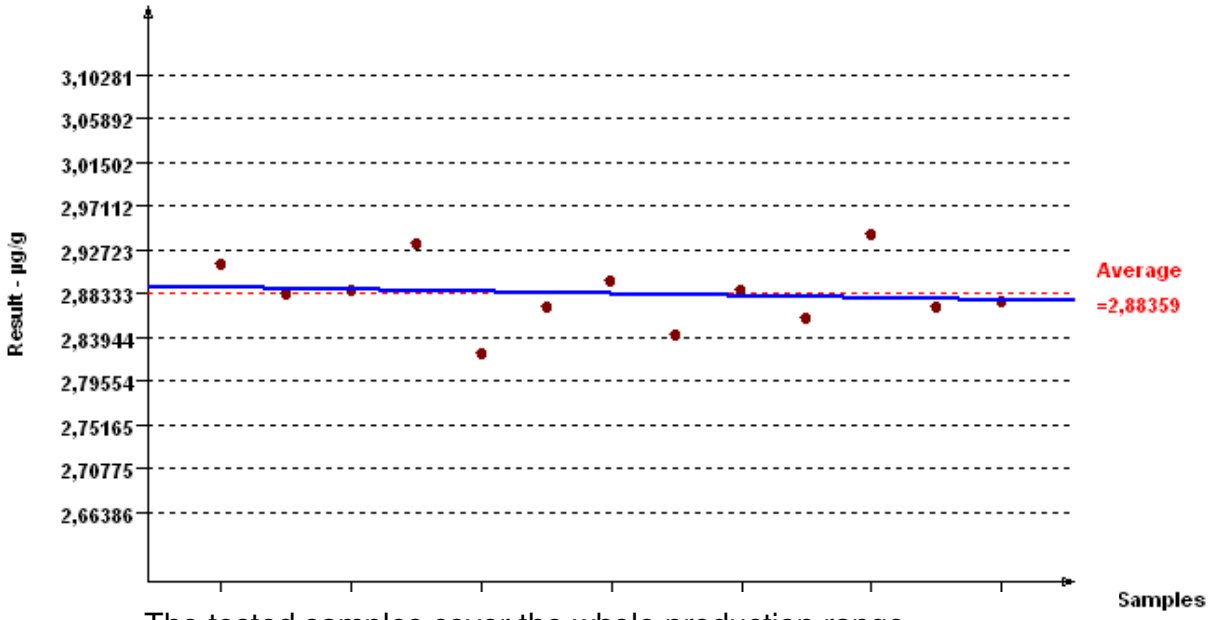
The tested samples cover the whole production range

Benzo[*g,h,i*]perylene – Graph sample means



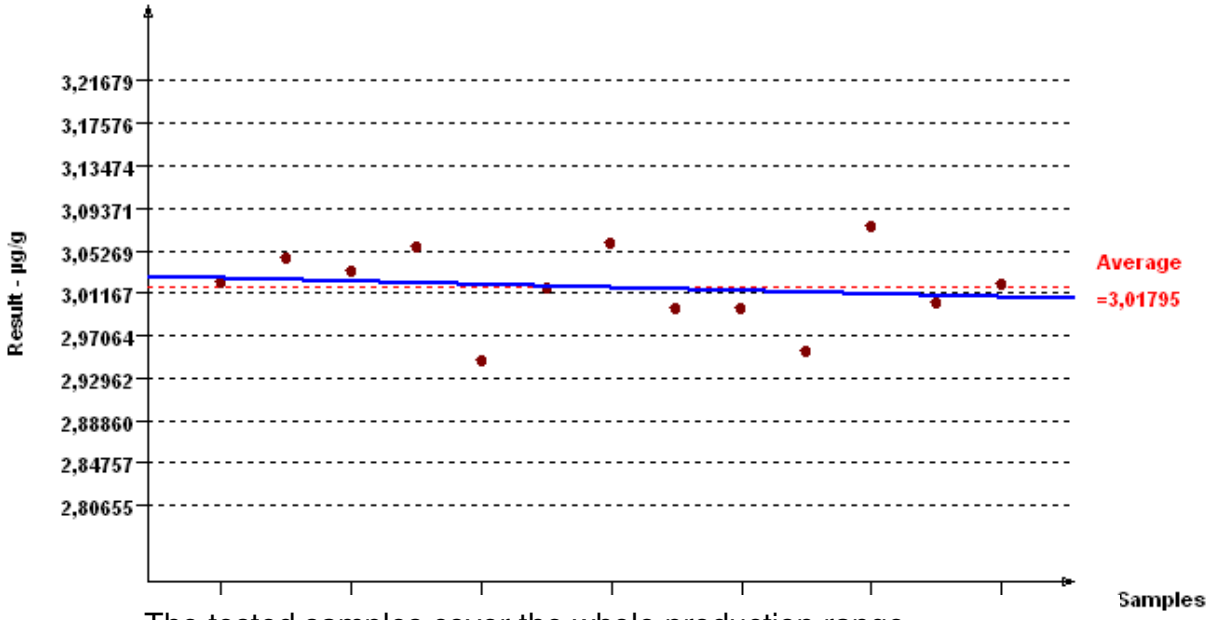
The tested samples cover the whole production range

Dibenzo[*a,l*]pyrene – Graph sample means



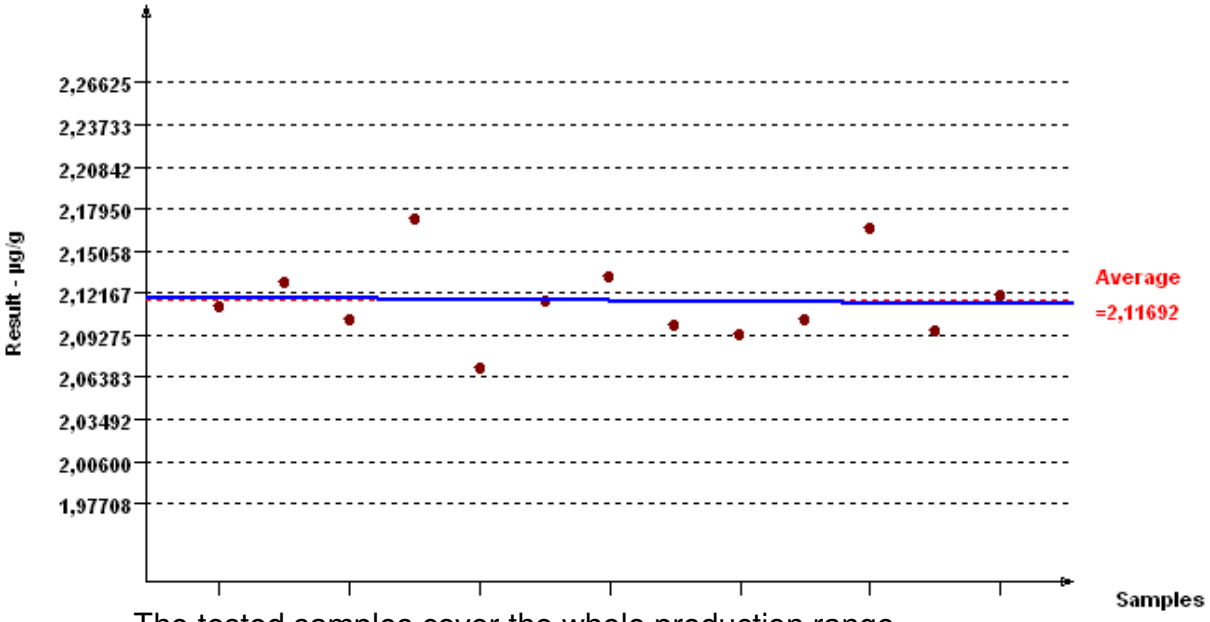
The tested samples cover the whole production range

Dibenzo[*a,e*]pyrene – Graph sample means



The tested samples cover the whole production range

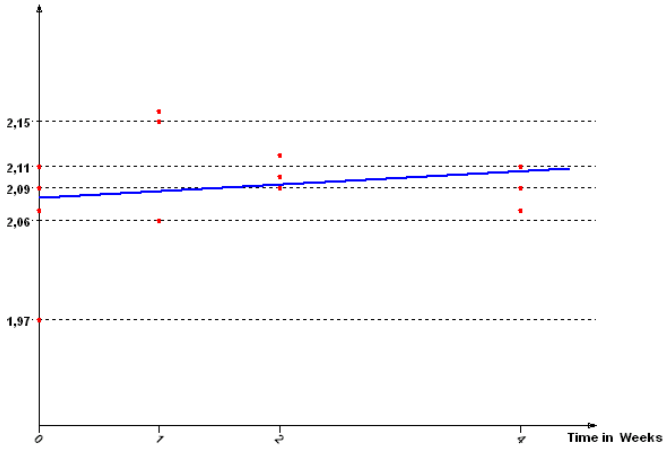
Dibenzo[*a,i*]pyrene – Graph sample means



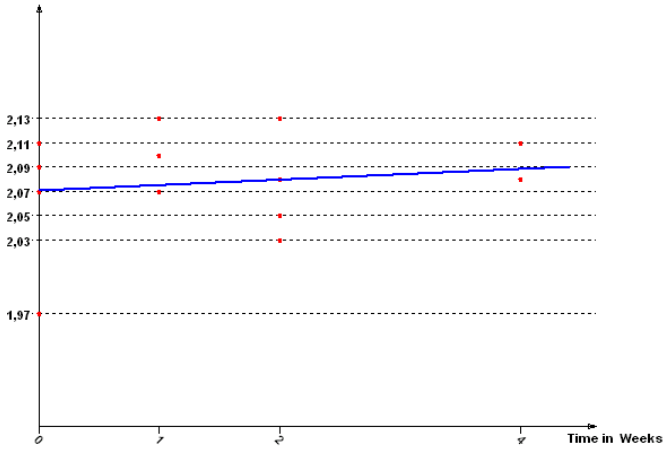
The tested samples cover the whole production range

ANNEX B. Short-term stability data

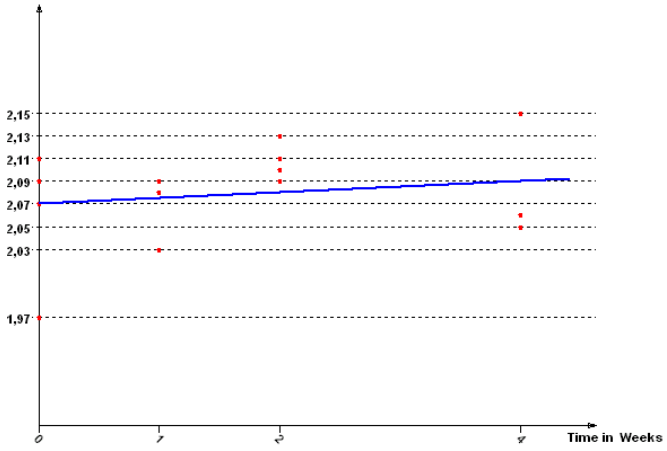
Benzo[c]fluorene - T=4°C



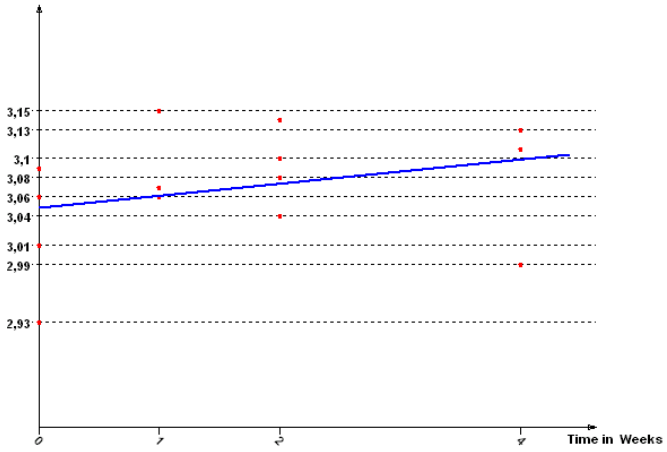
Benzo[c]fluorene - T=18°C



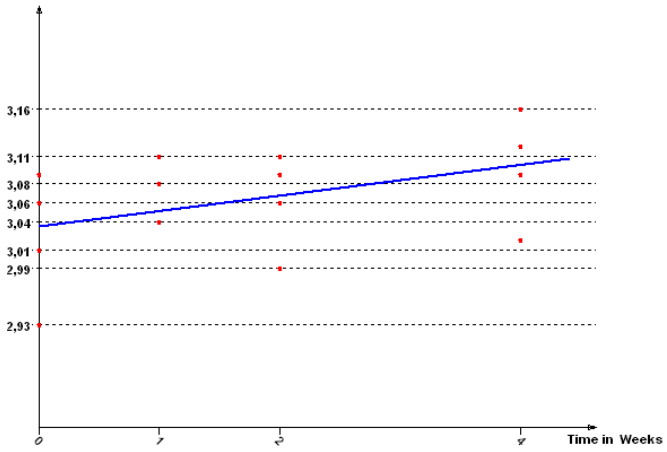
Benzo[c]fluorene - T=60°C



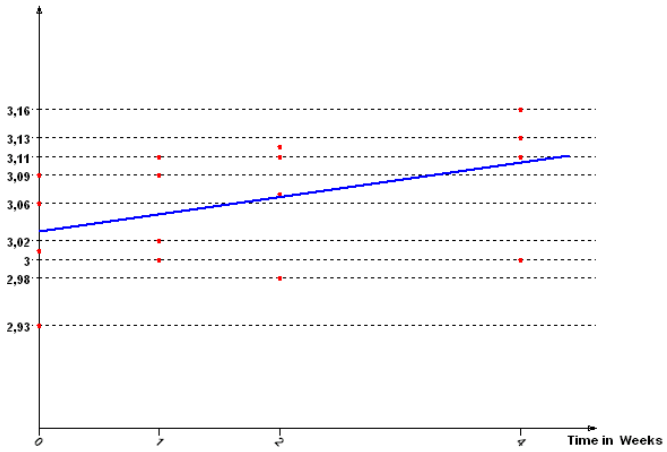
Benz[a]anthracene - T=4°C



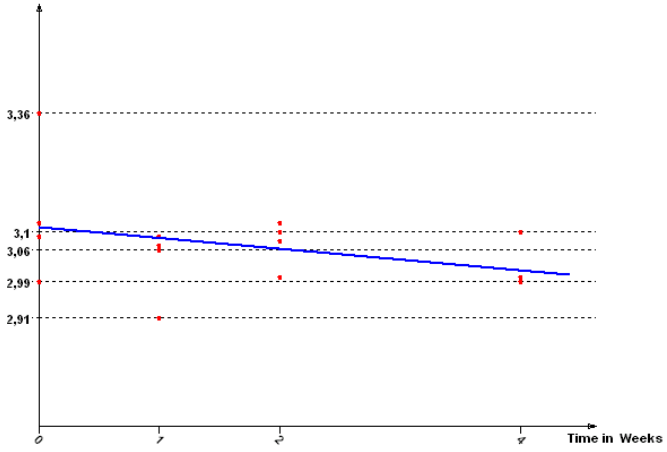
Benz[a]anthracene - T=18°C



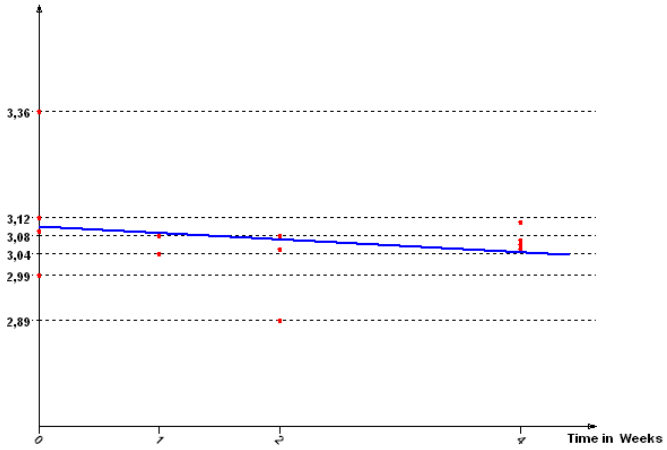
Benz[a]anthracene - T=60°C



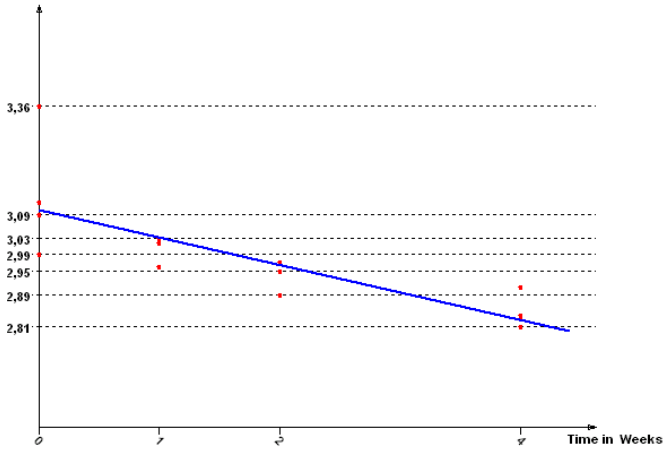
Cyclopenta[cd]pyrene - T=4°C



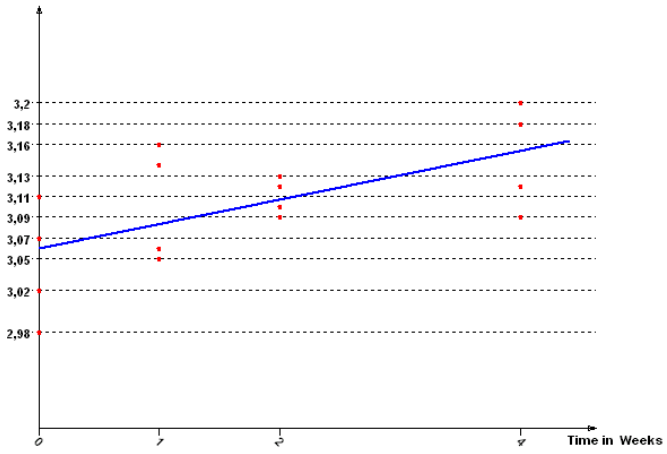
Cyclopenta[cd]pyrene - T=18°C



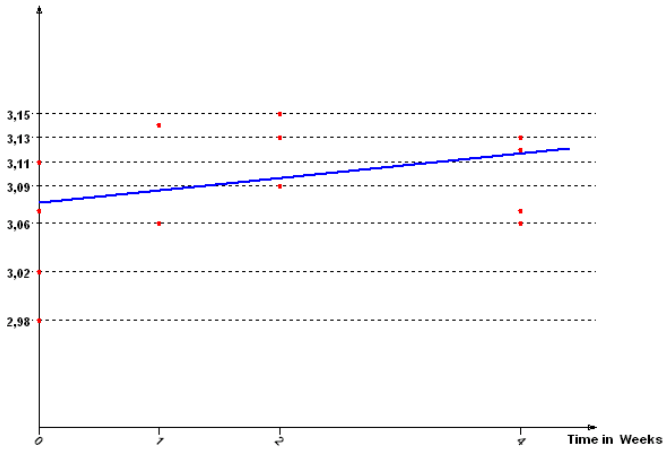
Cyclopenta[cd]pyrene - T=60°C



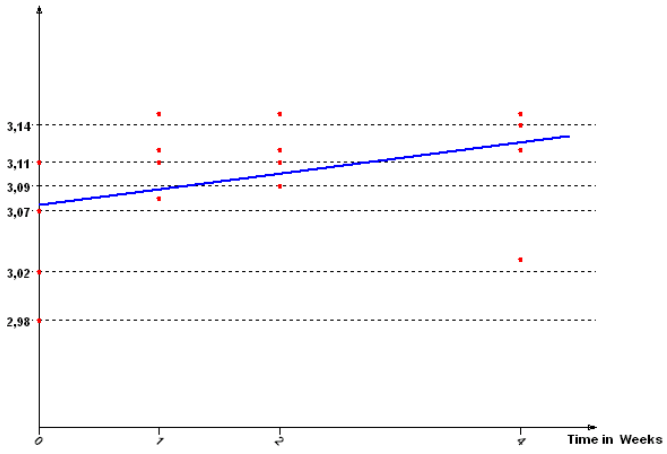
Chrysene - T=4°C



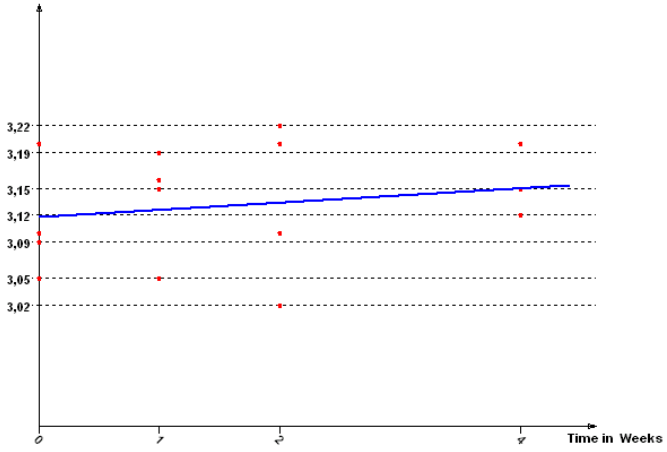
Chrysene - T=18°C



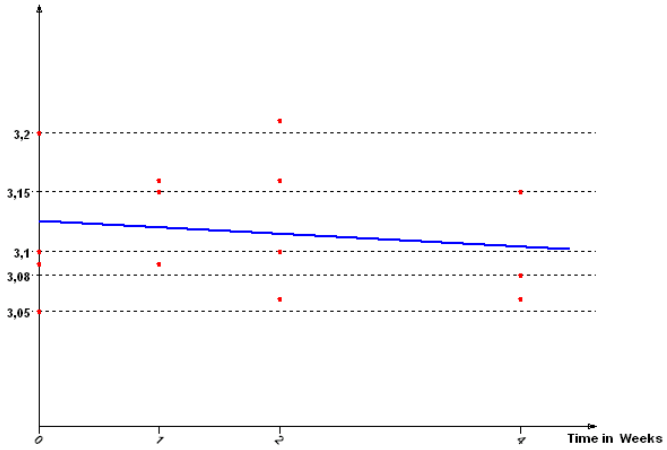
Chrysene - T=60°C



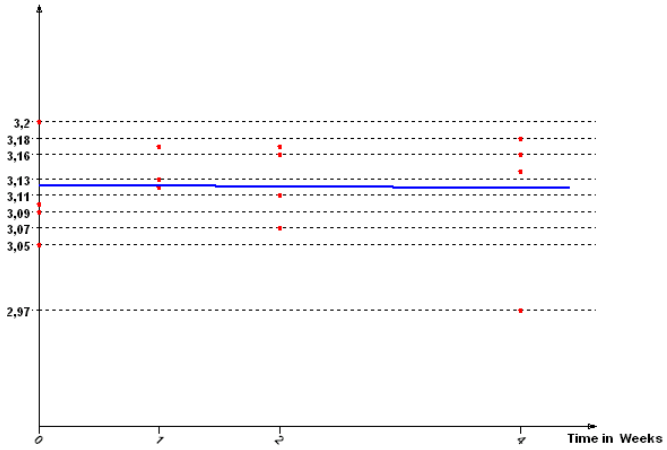
5-Methylchrysene - T=4°C



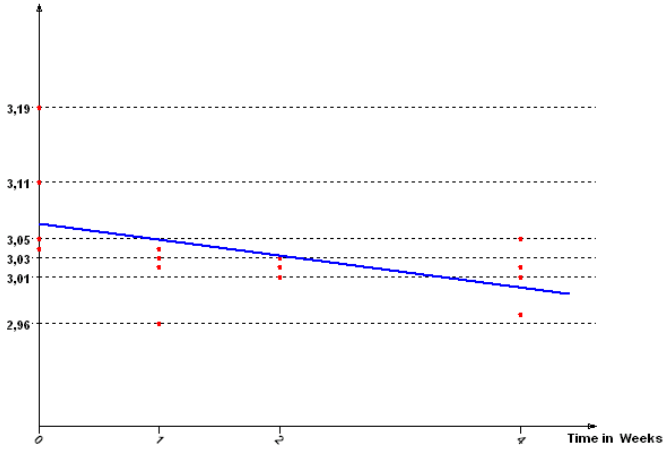
5-Methylchrysene - T=18°C



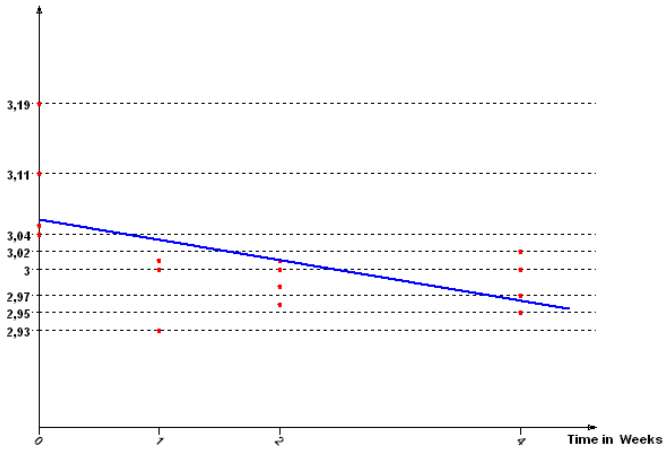
5-Methylchrysene - T=60°C



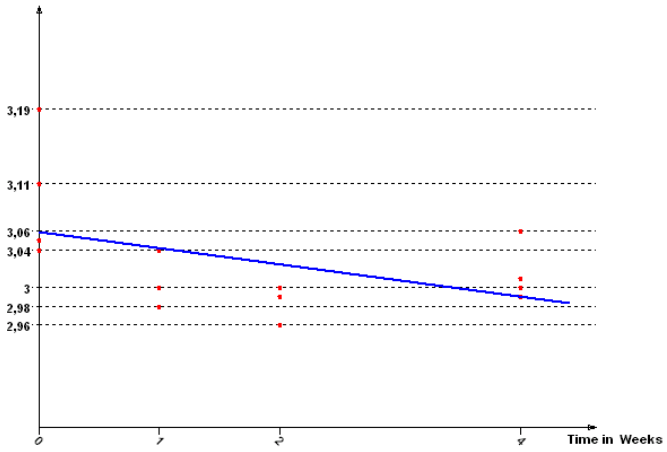
Benzo[b]fluoranthene - T=4°C



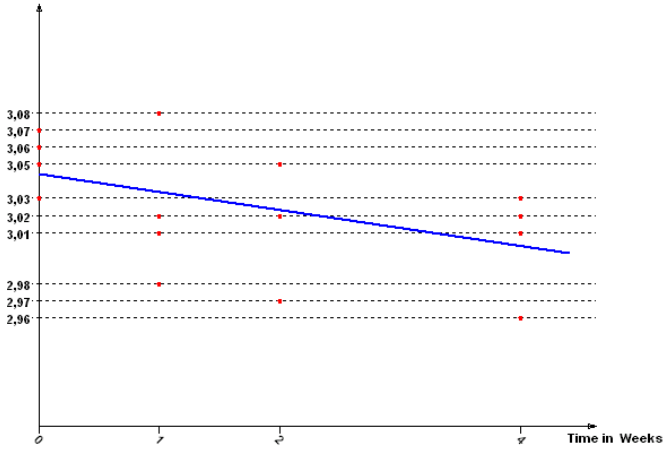
Benzo[b]fluoranthene - T=18°C



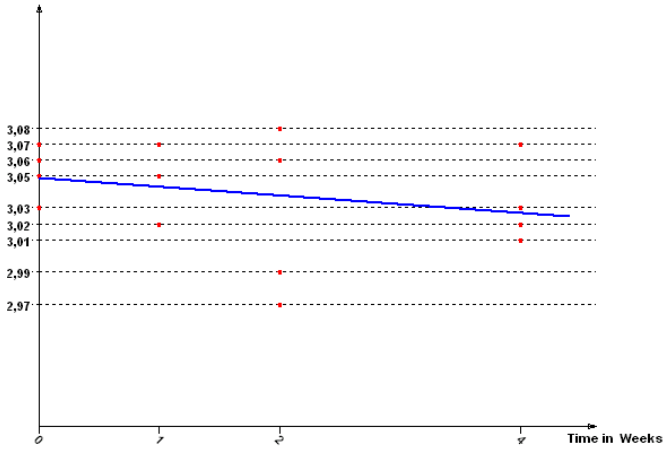
Benzo[b]fluoranthene - T=60°C



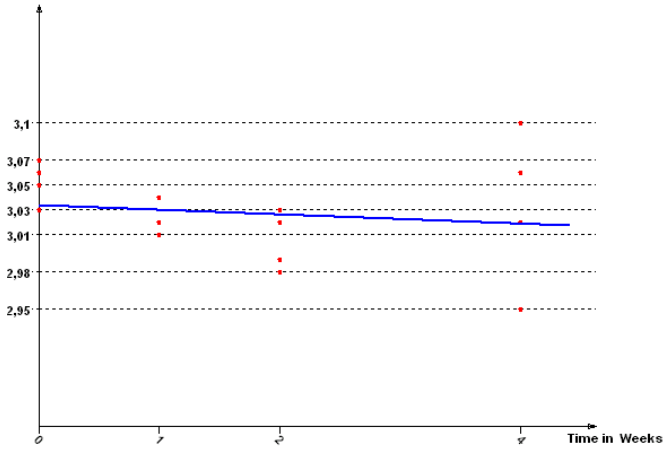
Benzo[k]fluoranthene - T=4°C



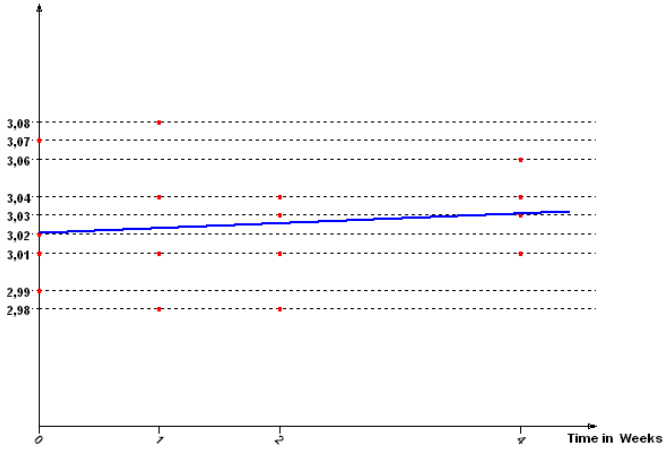
Benzo[k]fluoranthene - T=18°C



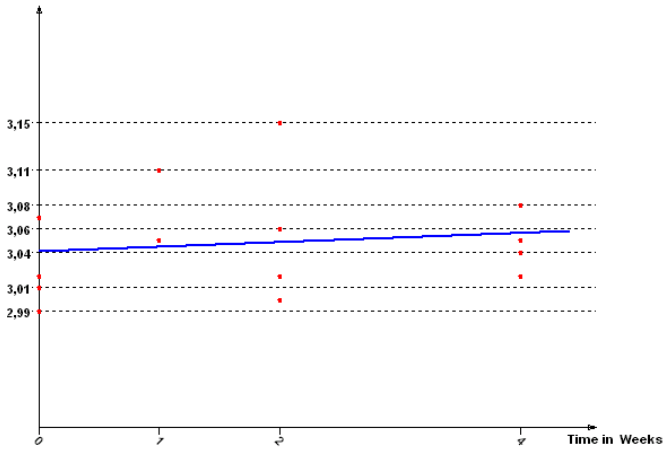
Benzo[k]fluoranthene - T=60°C



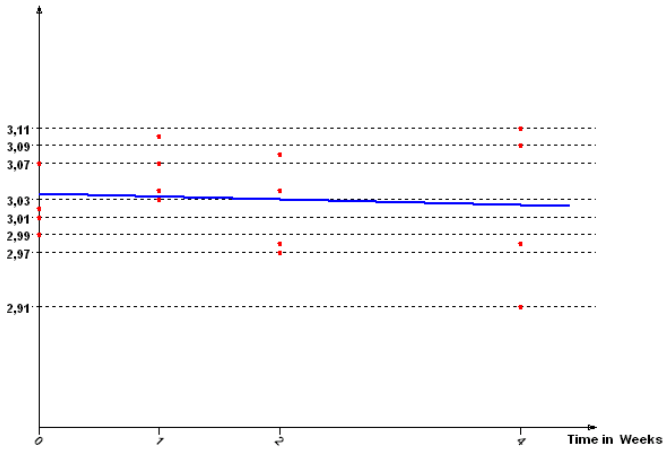
Benzo[j]fluoranthene T=4°C



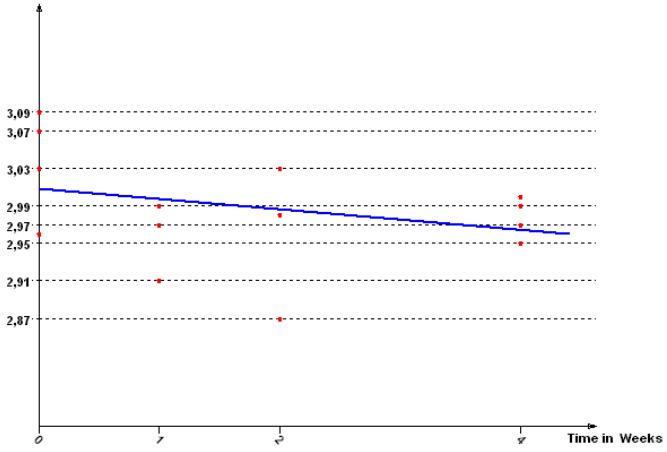
Benzo[j]fluoranthene T=18°C



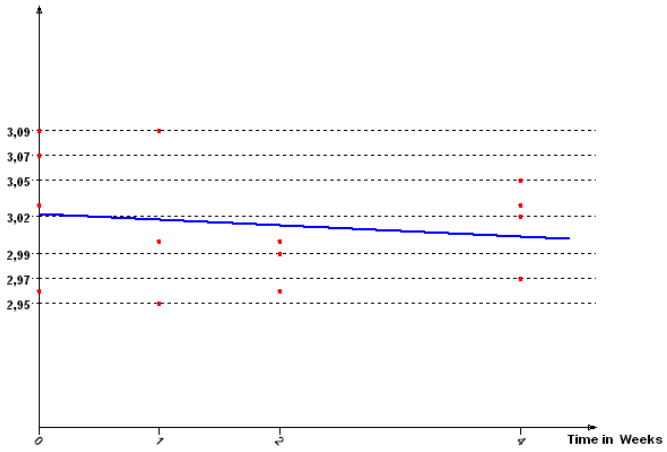
Benzo[j]fluoranthene T=60°C



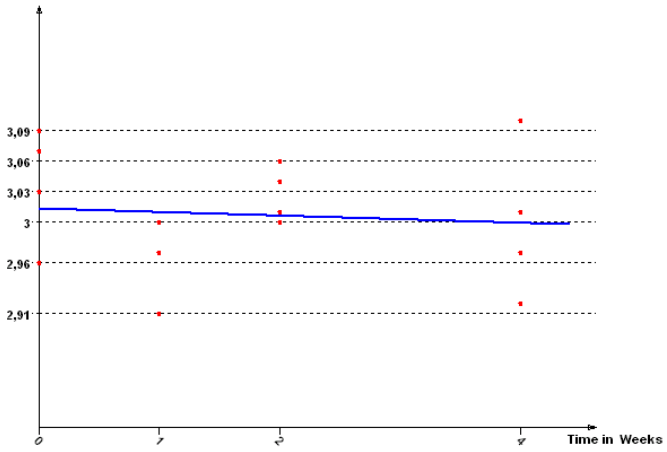
Benzo[a]pyrene T=4°C



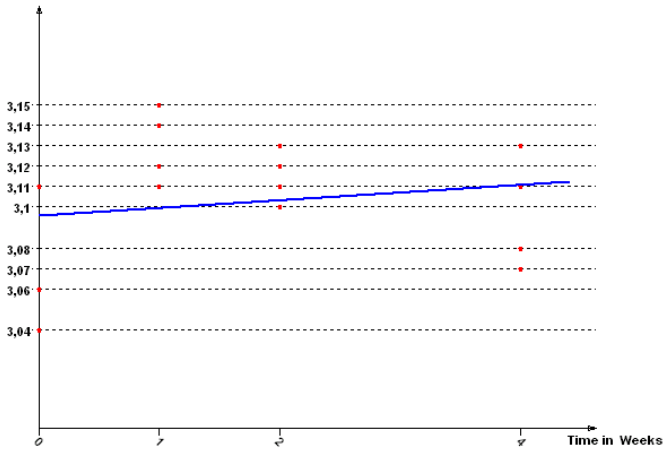
Benzo[a]pyrene T=18°C



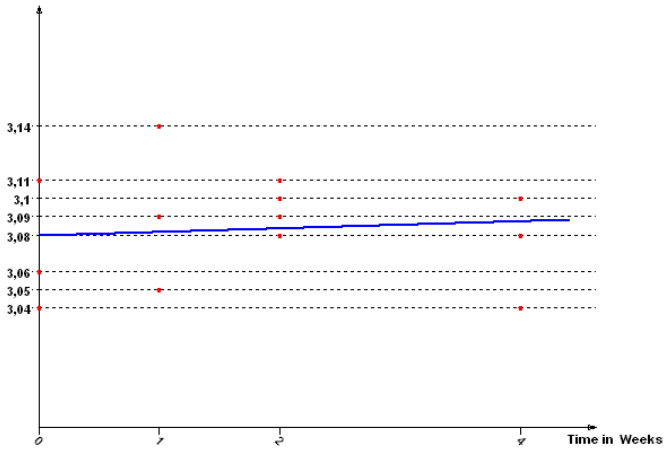
Benzo[a]pyrene T=18°C



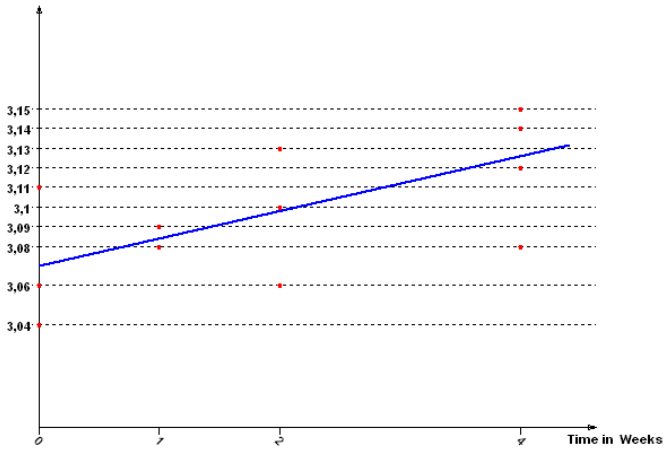
Indeno[1,2,3-cd]pyrene - T=4°C



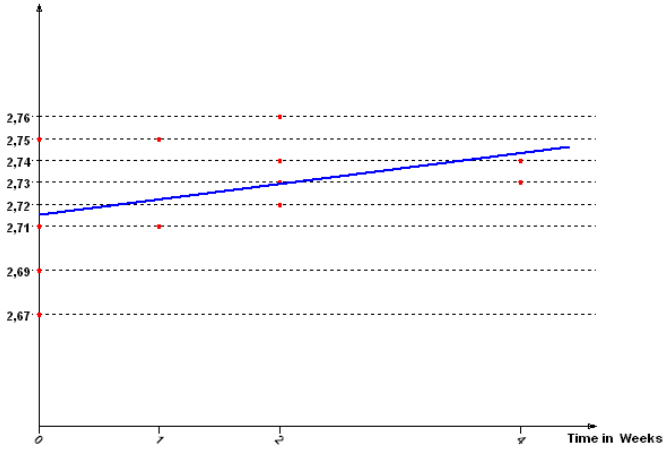
Indeno[1,2,3-cd]pyrene - T=18°C



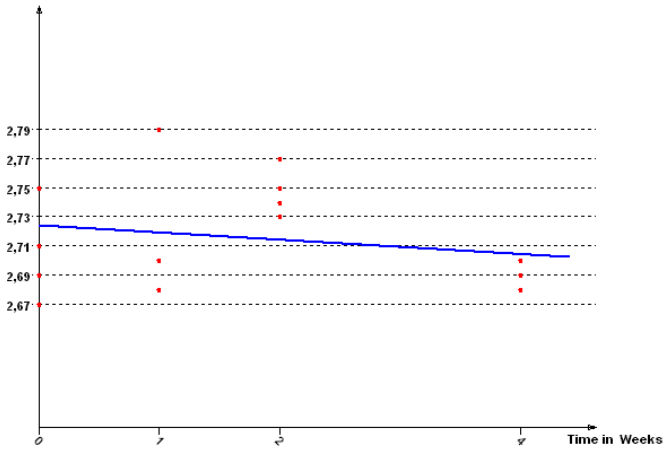
Indeno[1,2,3-cd]pyrene - T=60°C



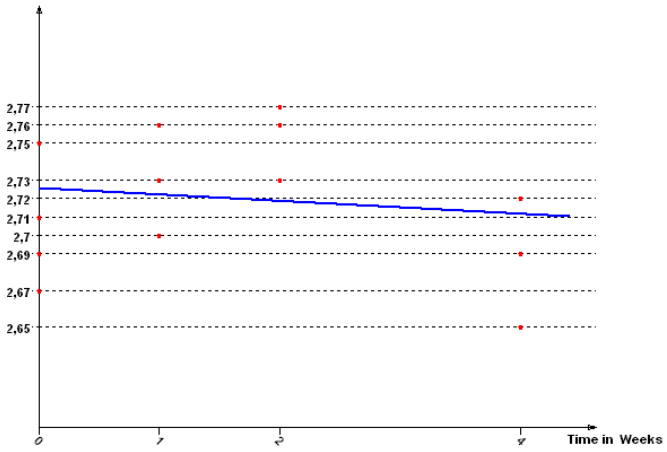
Dibenz[a,h]anthracene - T=4°C



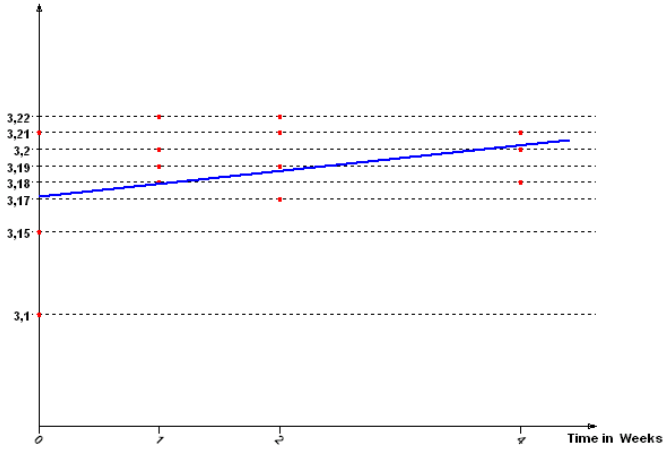
Dibenz[a,h]anthracene - T=18°C



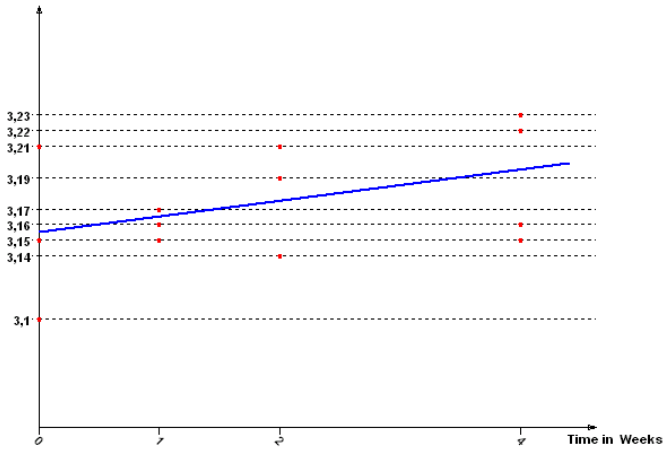
Dibenz[a,h]anthracene - T=60°C



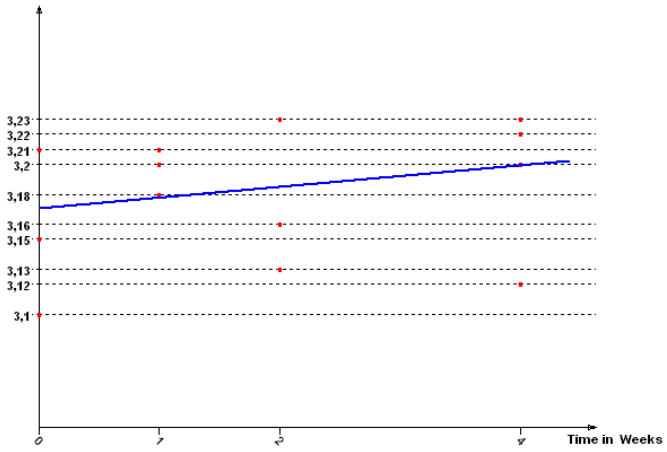
Benzo[ghi]perylene - T=4°C



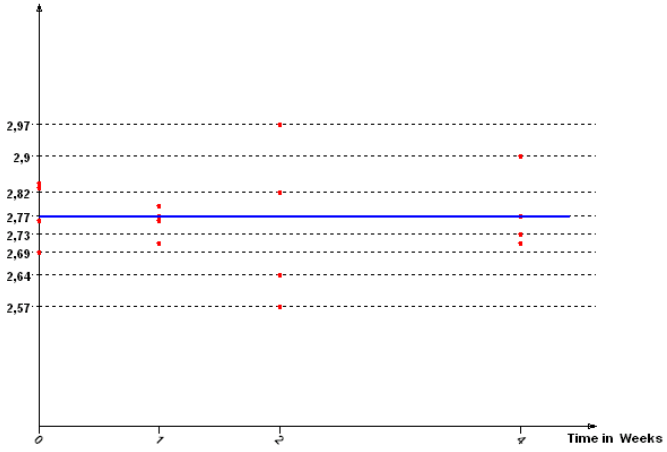
Benzo[ghi]perylene - T=18°C



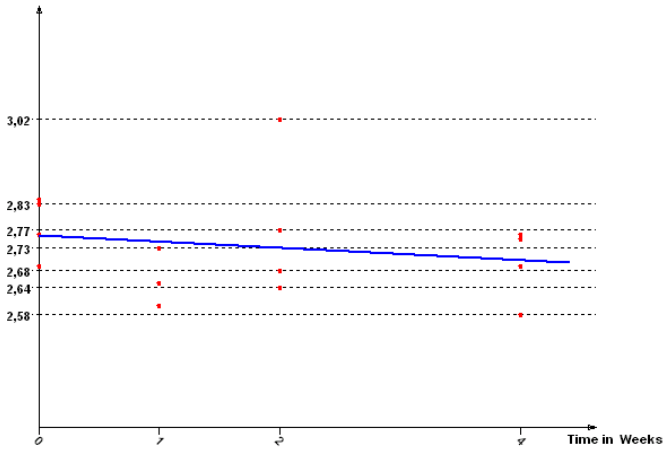
Benzo[ghi]perylene - T=60°C



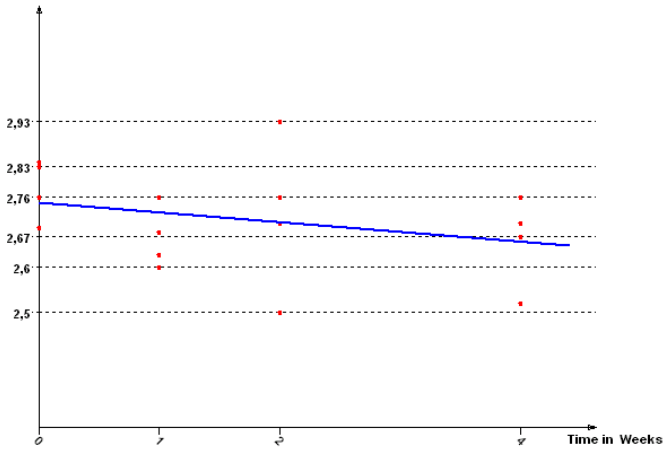
Dibenzo[a,l]pyrene - T=4°C



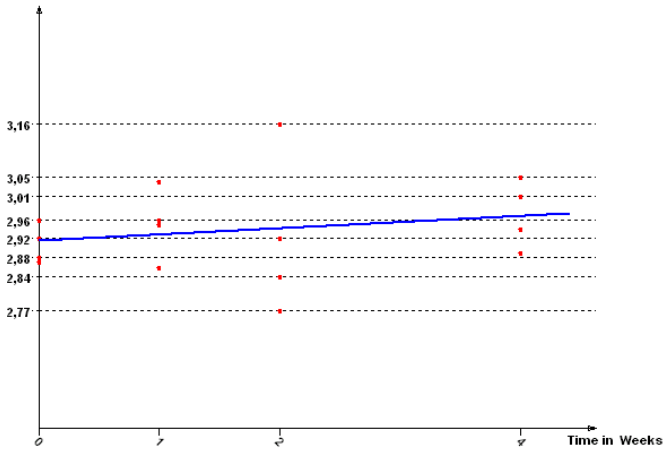
Dibenzo[a,l]pyrene - T=18°C



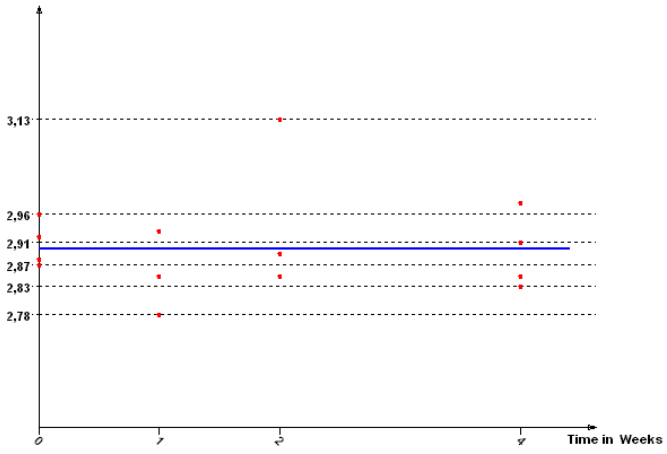
Dibenzo[a,l]pyrene - T=60°C



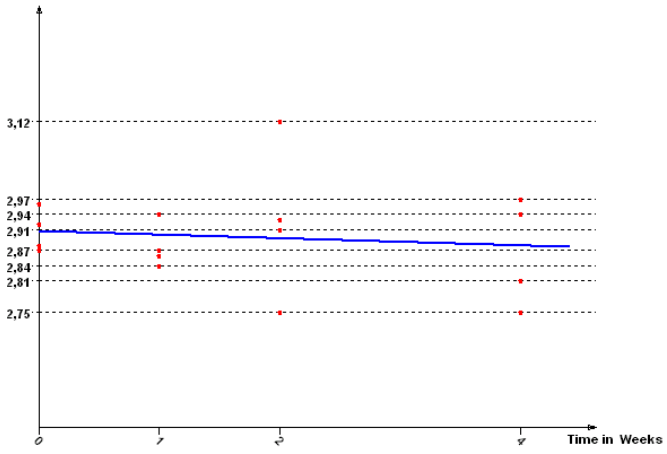
Dibenzo[a,e]pyrene - T=4°C



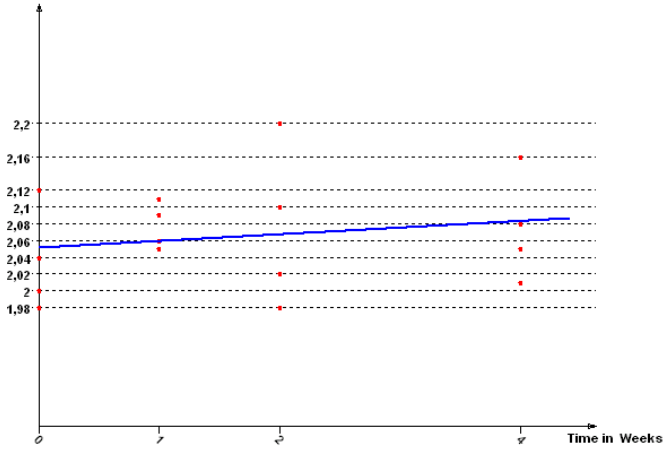
Dibenzo[a,e]pyrene - T=18°C



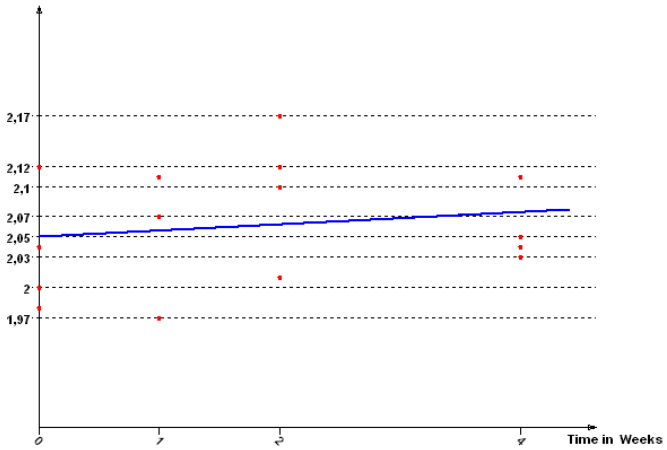
Dibenzo[a,e]pyrene - T=60°C



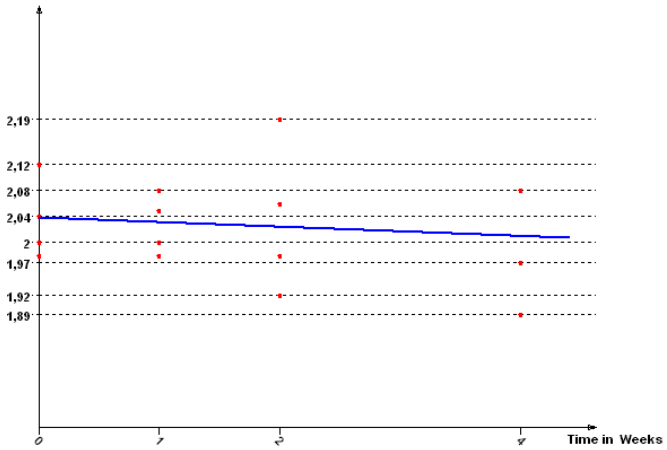
Dibenzo[a,i]pyrene - T=4°C



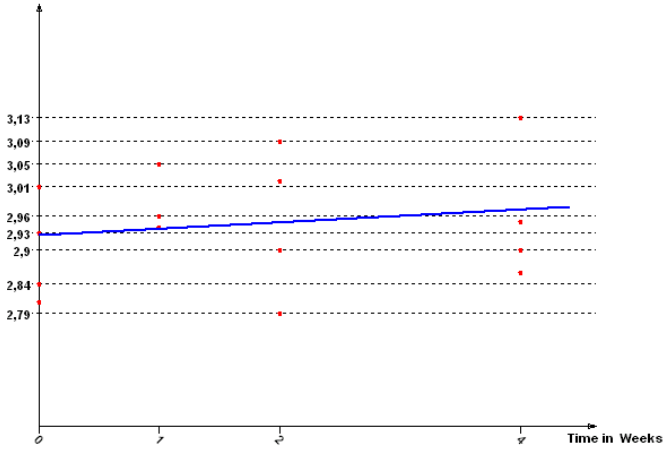
Dibenzo[a,i]pyrene - T=18°C



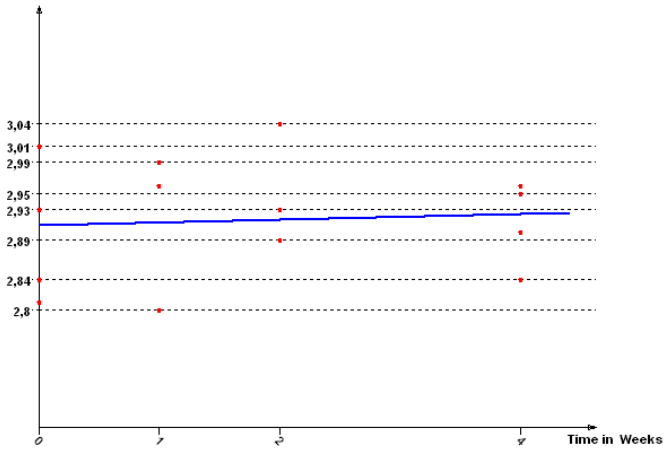
Dibenzo[a,i]pyrene - T=60°C



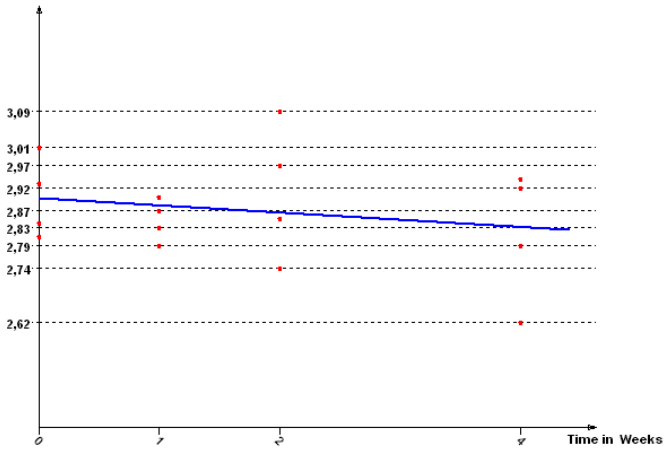
Dibenzo[a,h]pyrene - T=4°C



Dibenzo[a,h]pyrene - T=18°C

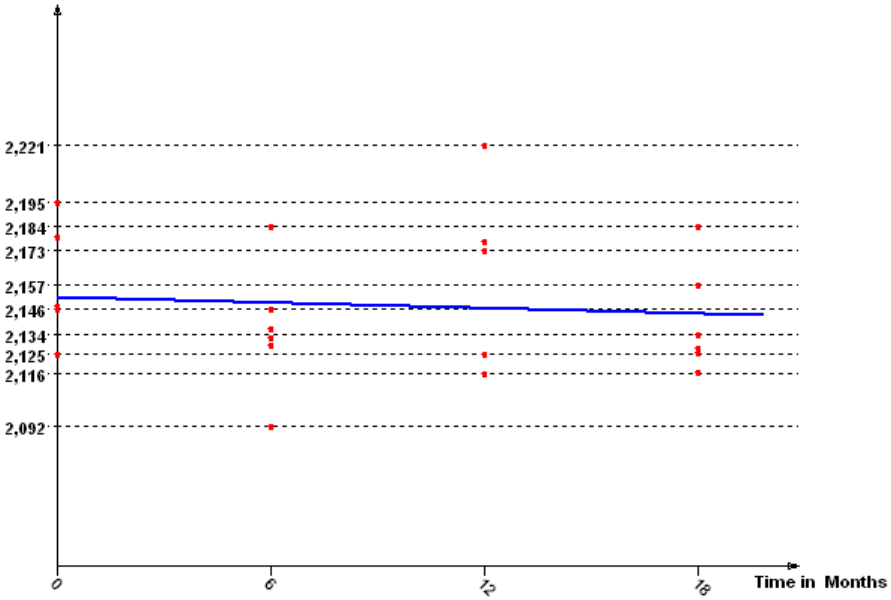


Dibenzo[a,h]pyrene - T=60°C

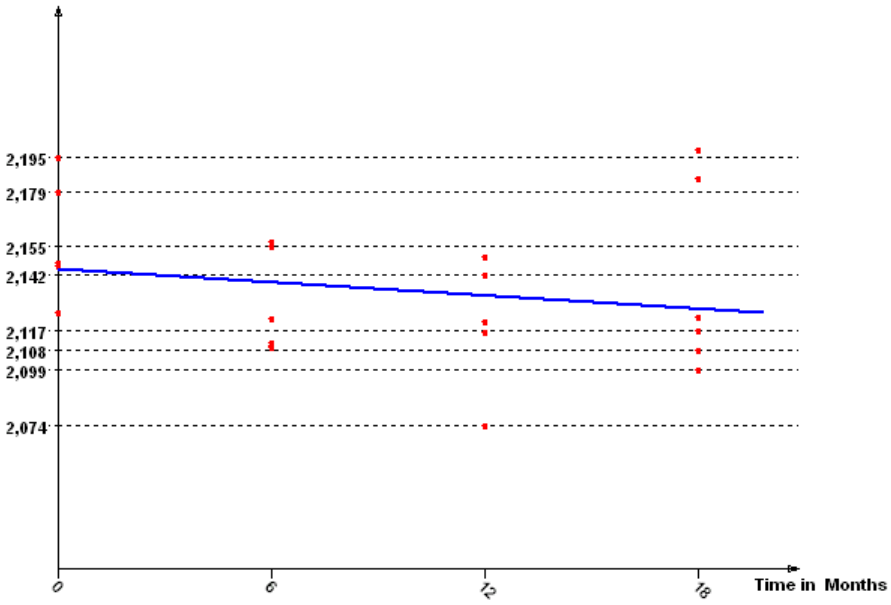


ANNEX C. Long-term stability data

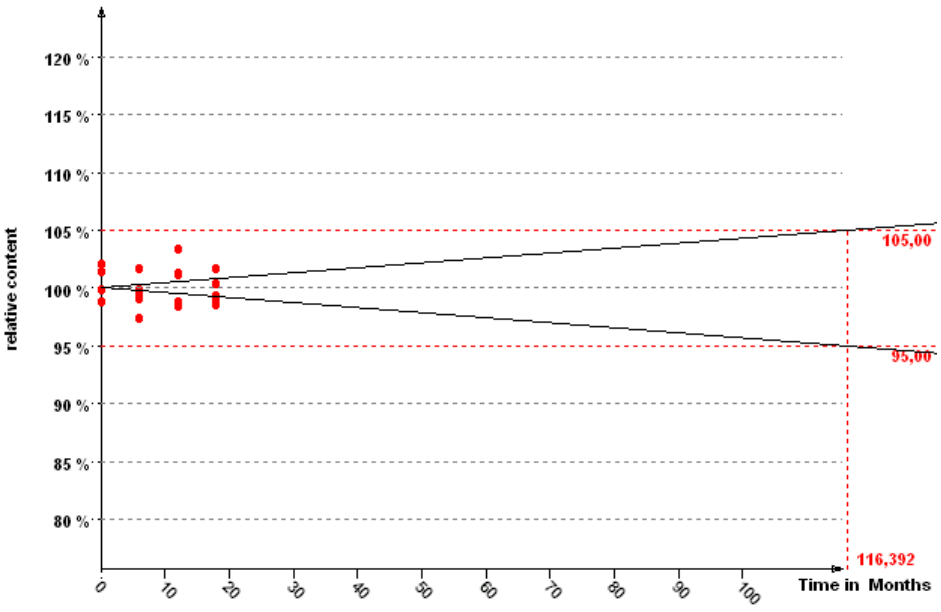
Benzo[c]fluorene - T=4°C



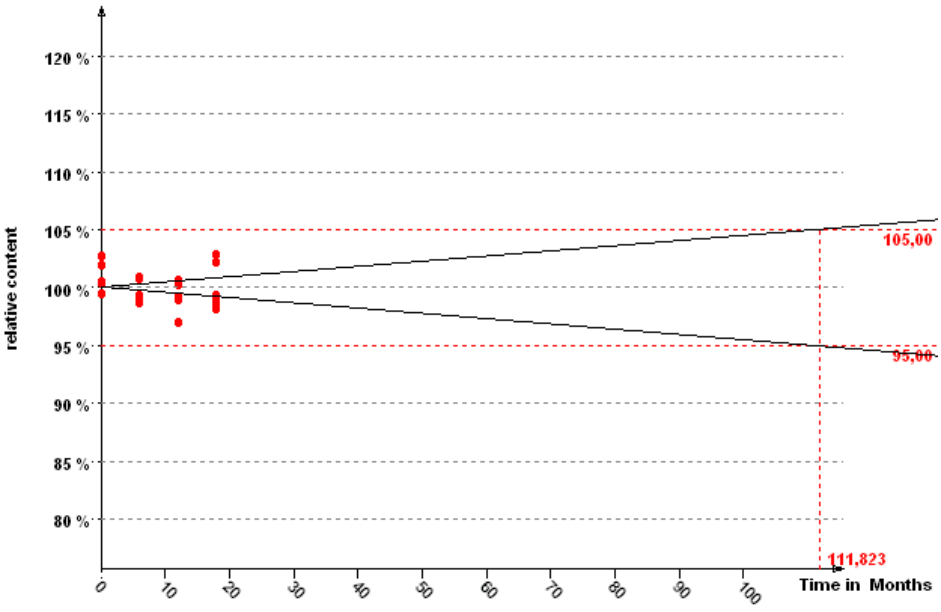
Benzo[c]fluorene - T=18°C



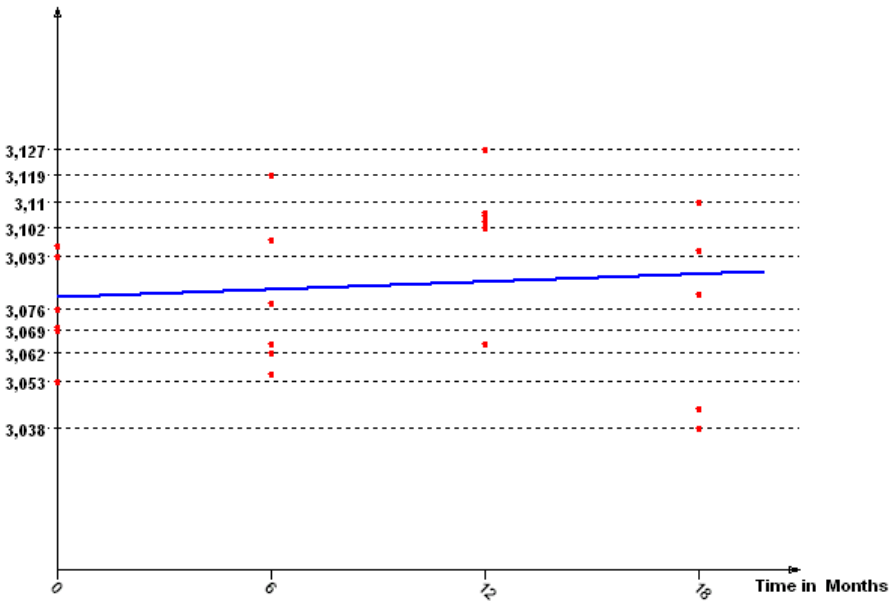
Shelf Life and Associated Ults, T=+4 °C



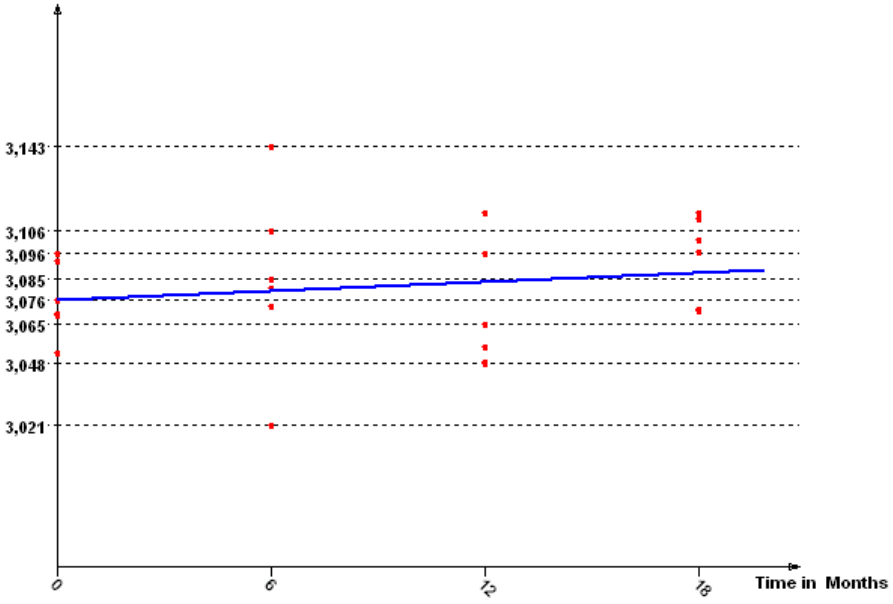
Shelf Life and Associated Ults, T=+18 °C



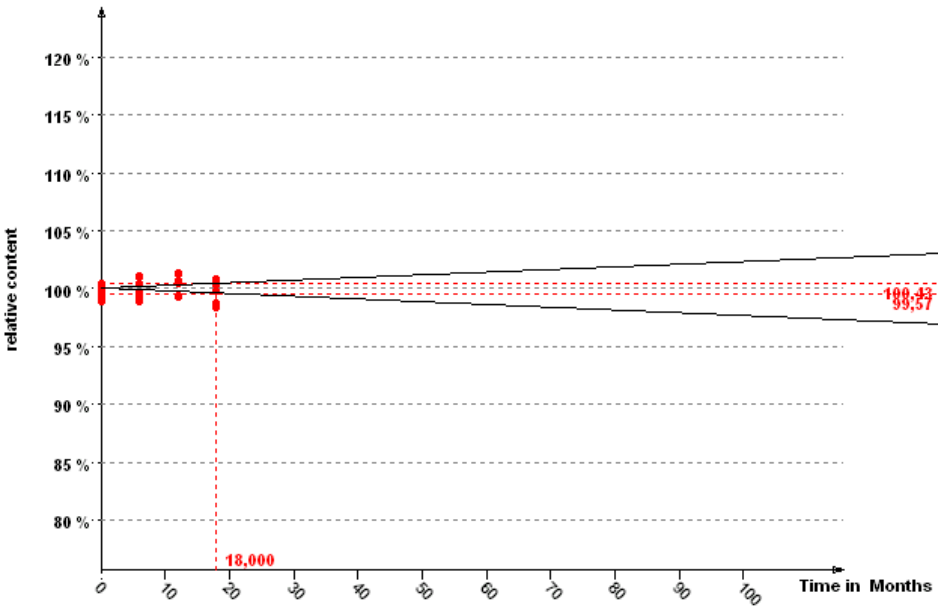
Benz[a]anthracene T=4°C



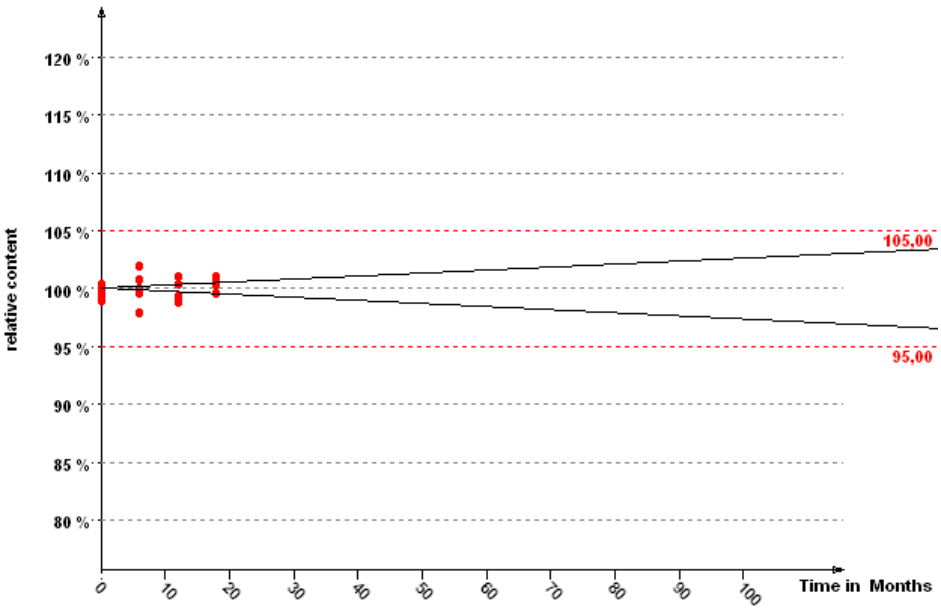
Benz[a]anthracene T=18°C



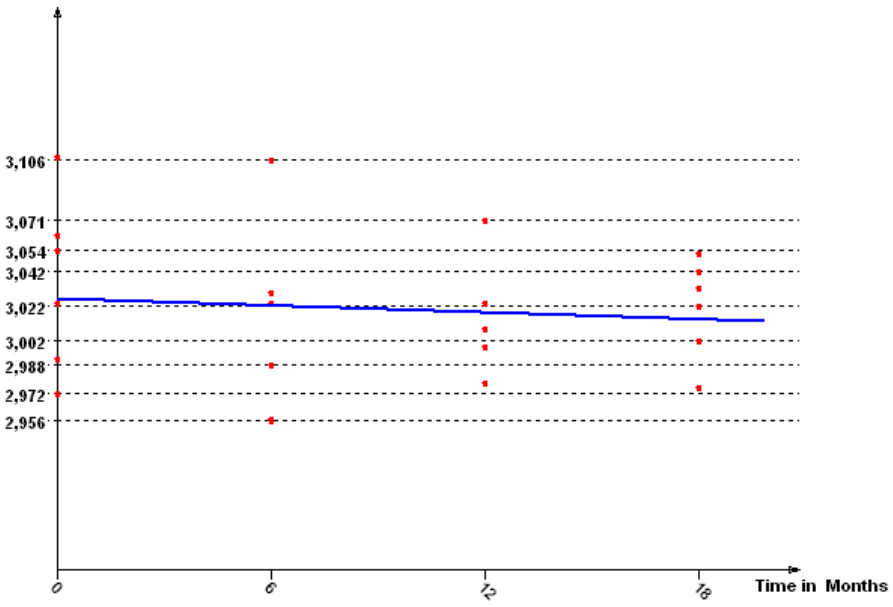
Shelf Life and Associated Ults, T=+4 °C



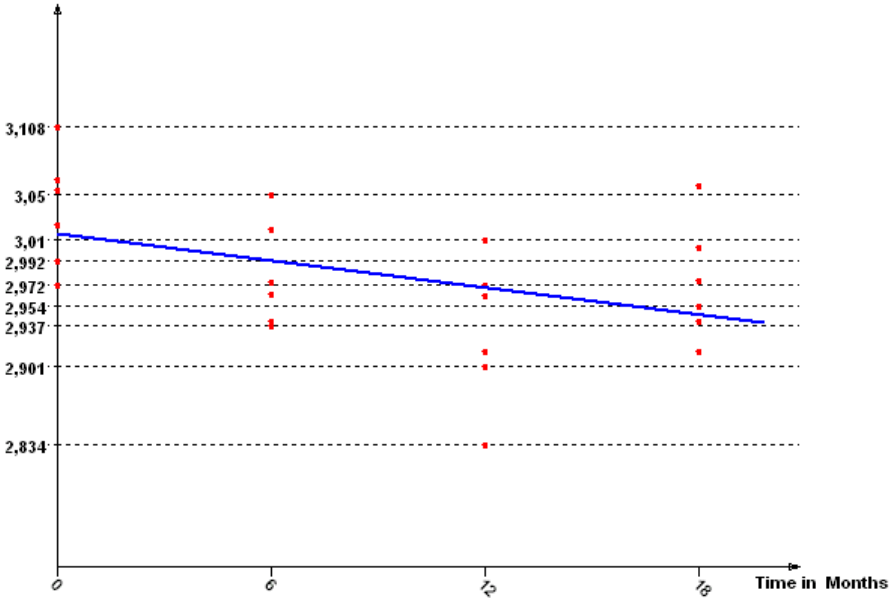
Shelf Life and Associated Ults, T=+18 °C



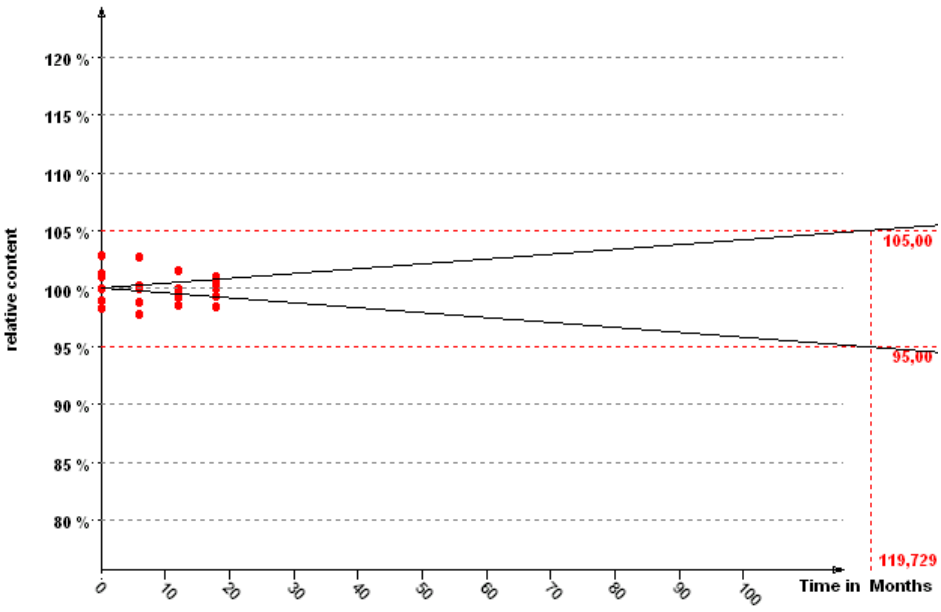
Cyclopenta[cd]pyrene - T=4°C



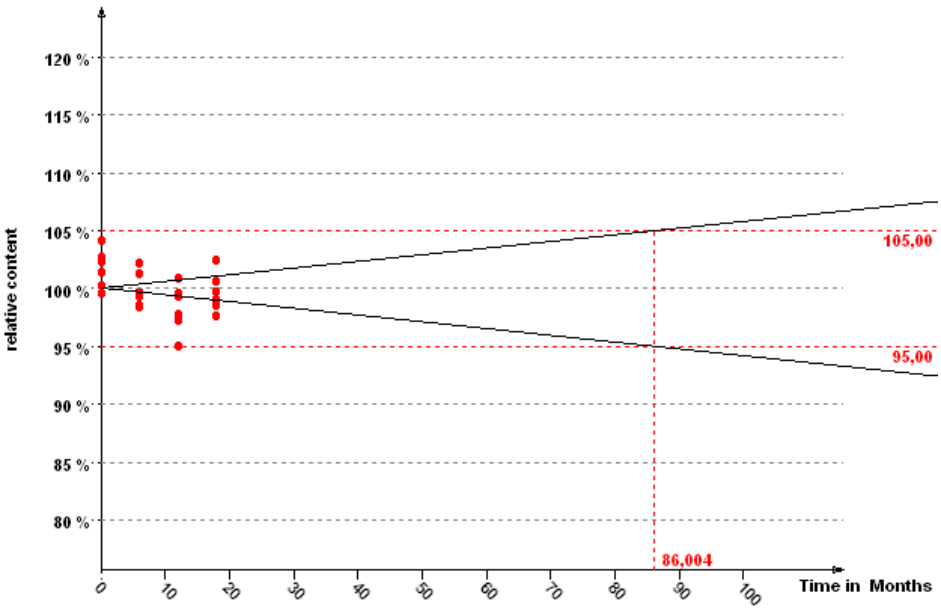
Cyclopenta[cd]pyrene - T=18°C



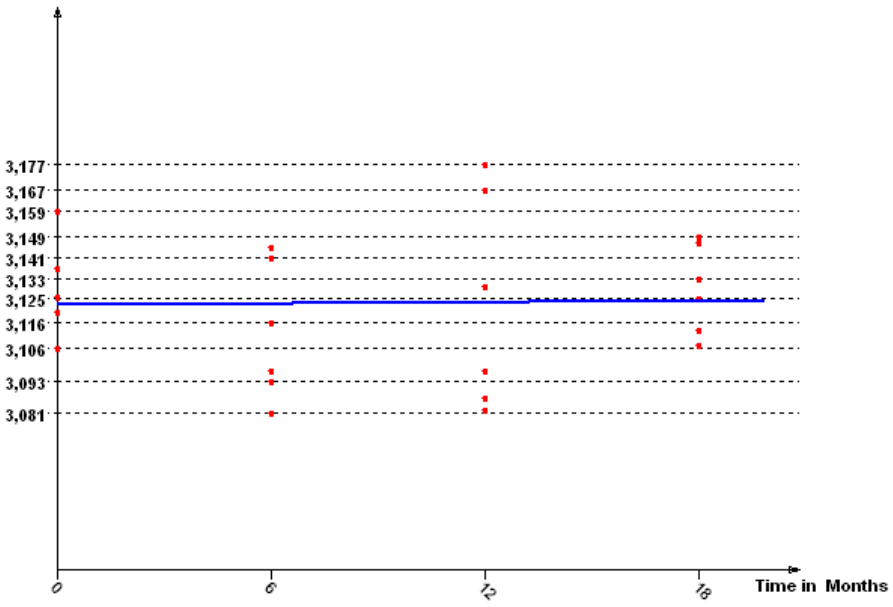
Shelf Life and Associated Ults, T=+4 °C



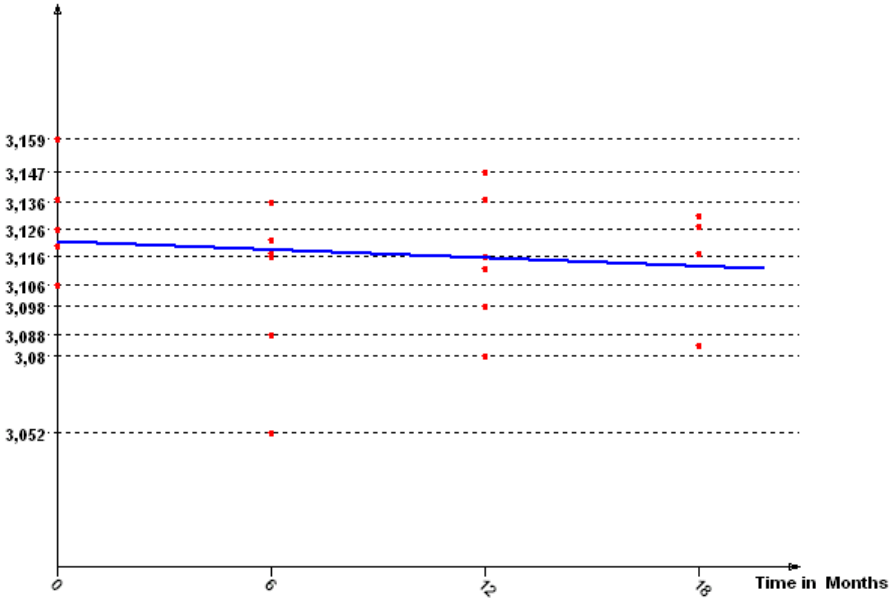
Shelf Life and Associated Ults, T=+18 °C



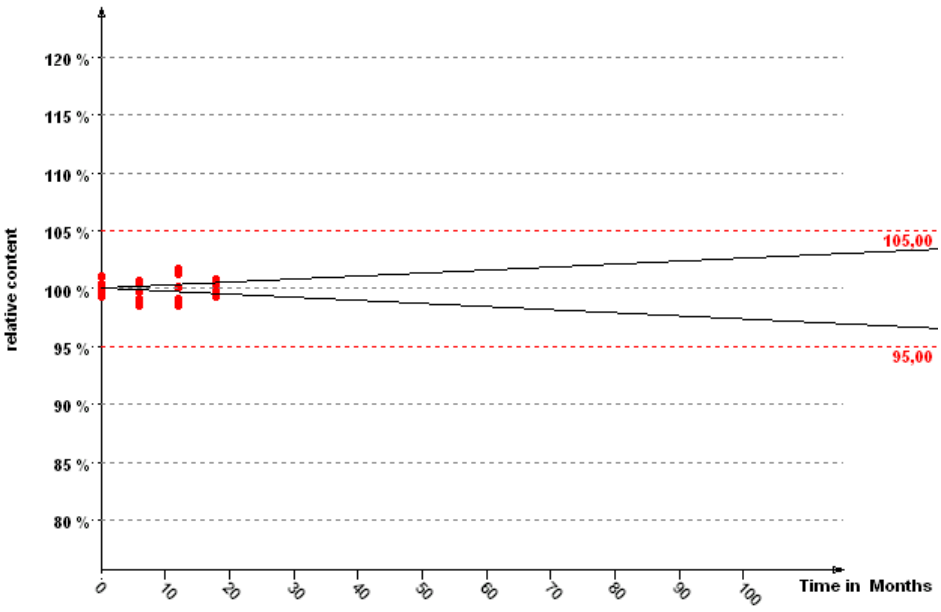
Chrysene - T=4°C



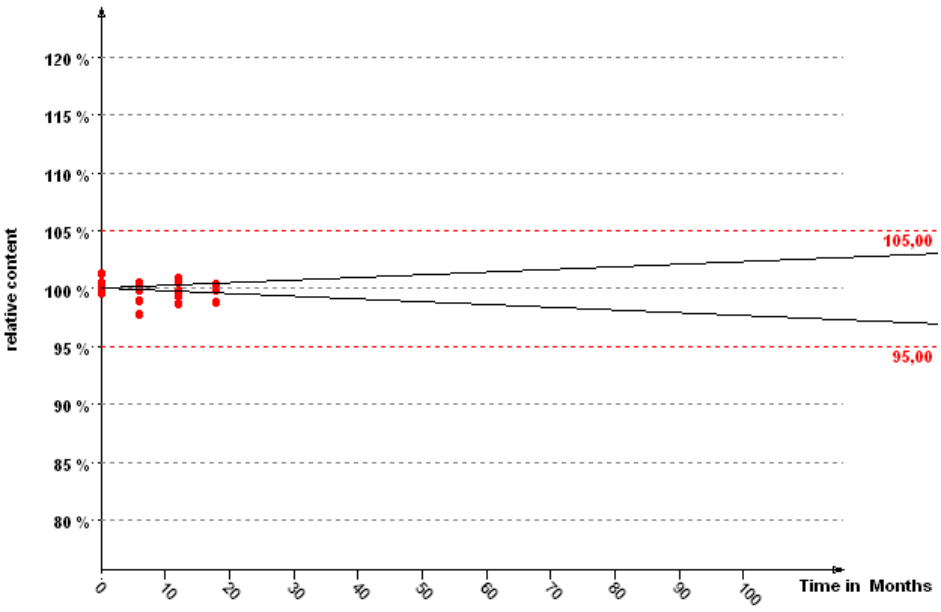
Chrysene - T=18°C



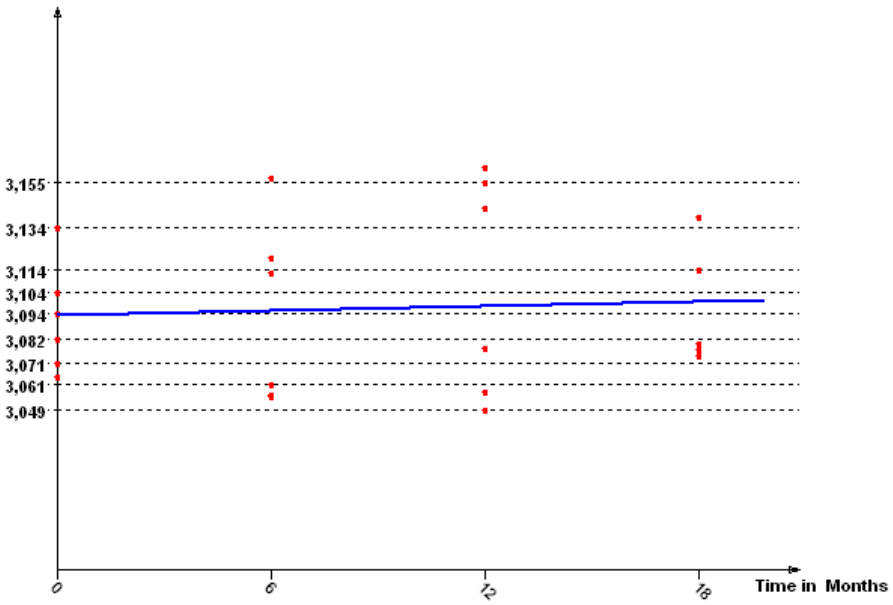
Shelf Life and Associated Ults, T=+4 °C



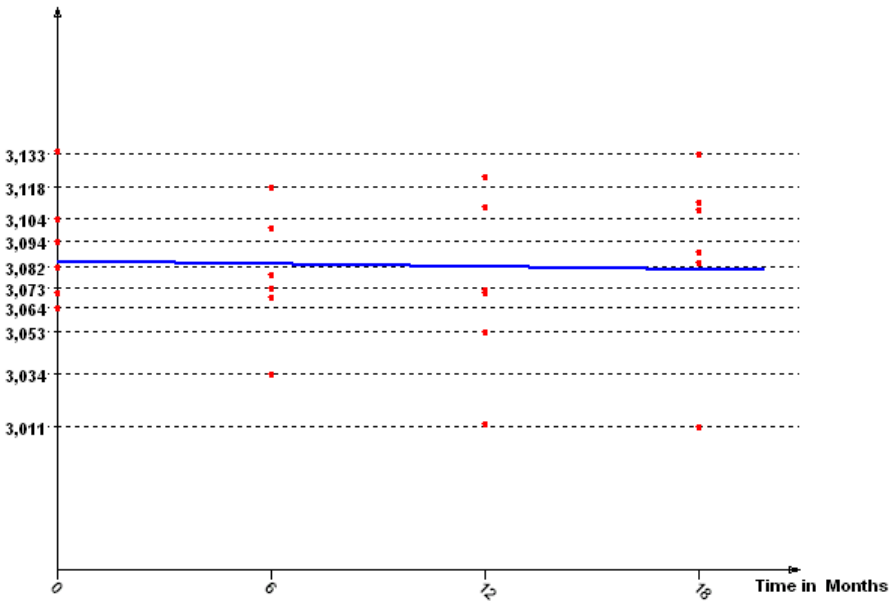
Shelf Life and Associated Ults, T=+18 °C



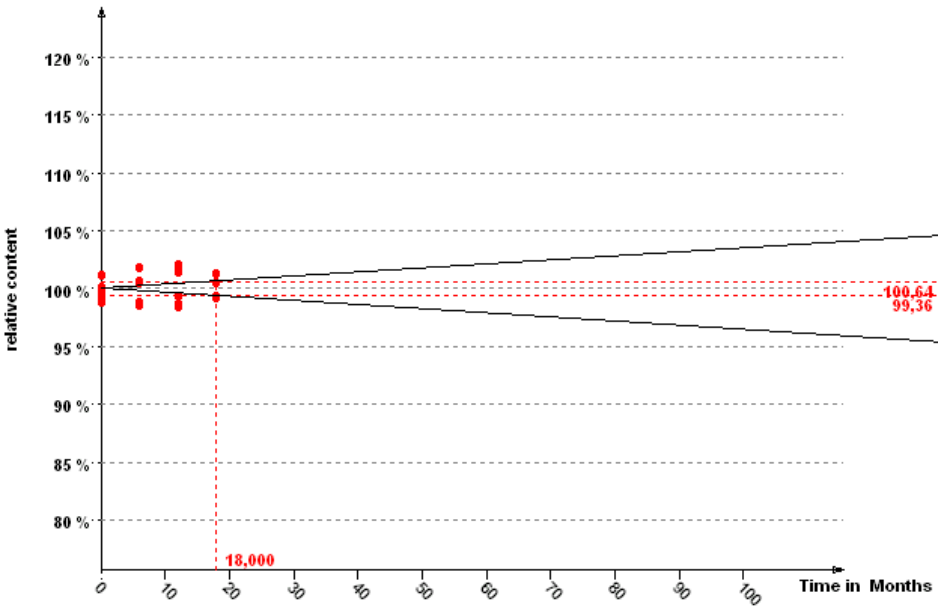
5-Methylchrysene - T=4°C



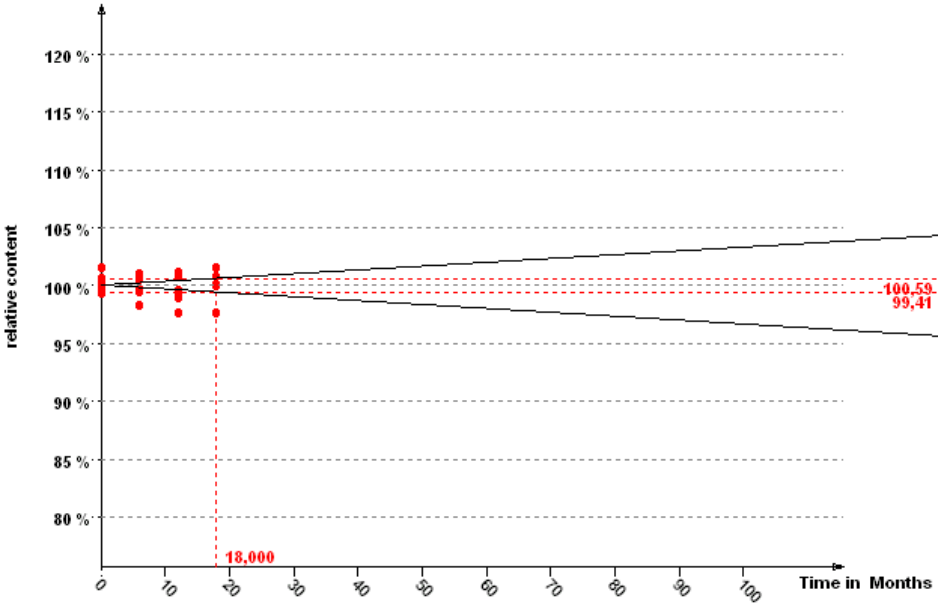
5-Methylchrysene - T=18°C



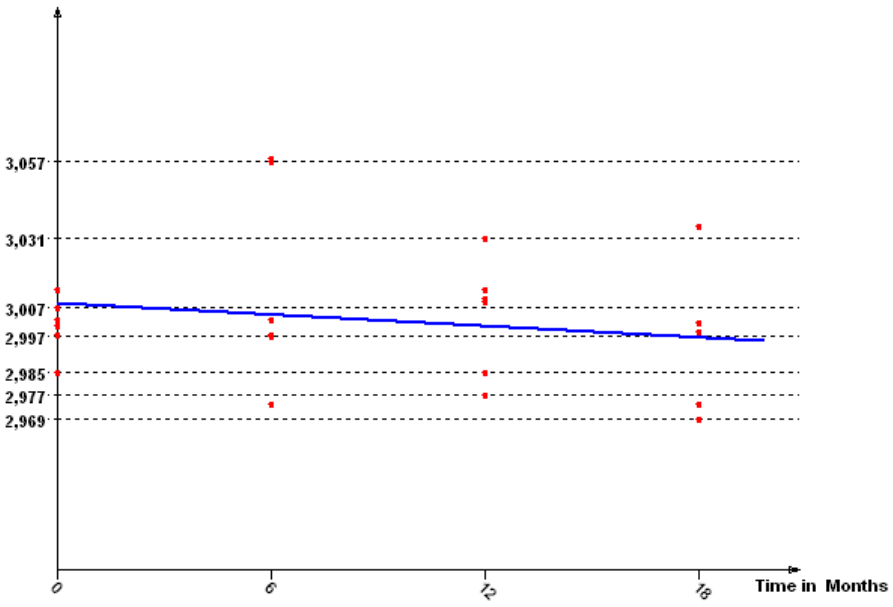
Shelf Life and Associated Ults, T=+4 °C



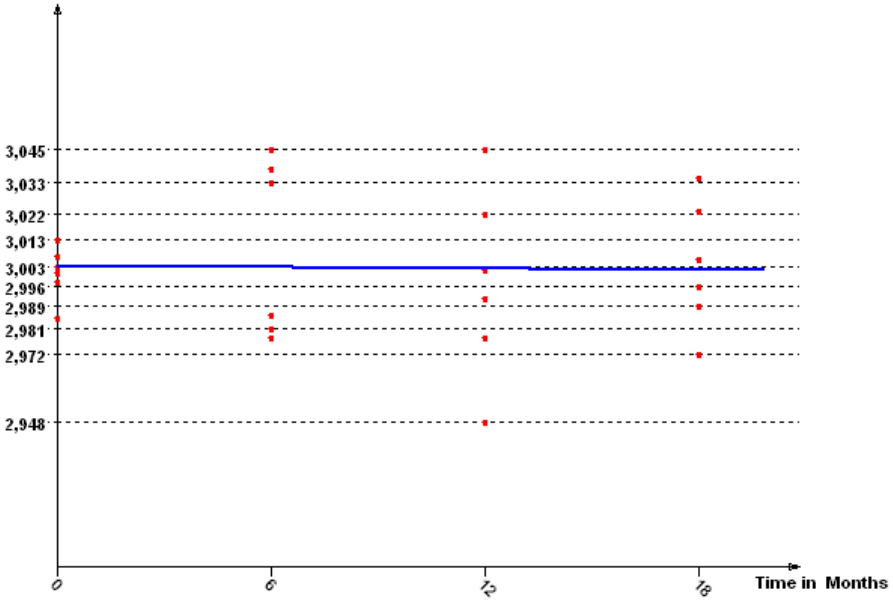
Shelf Life and Associated Ults, T=+18 °C



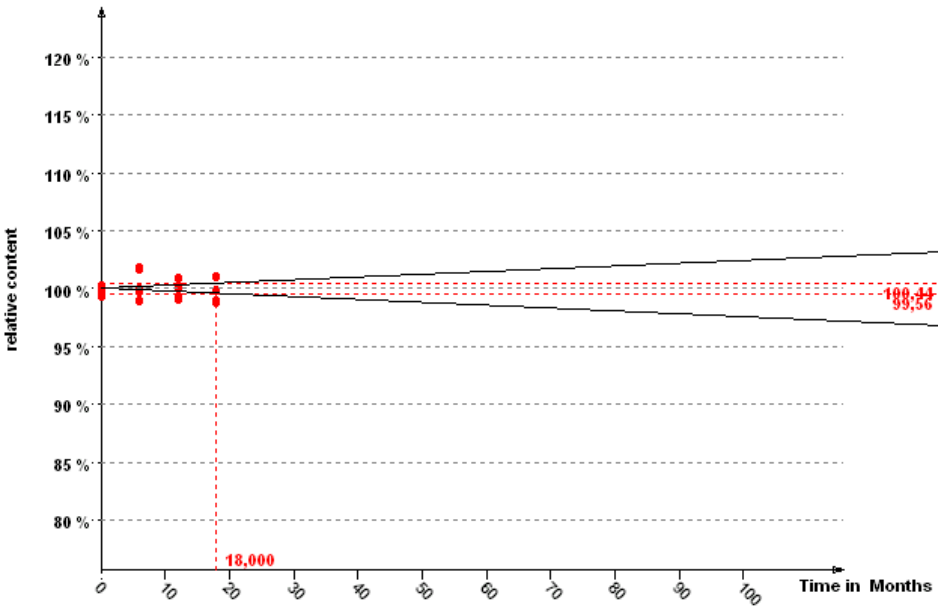
Benzo[b]fluoranthene - T=4°C



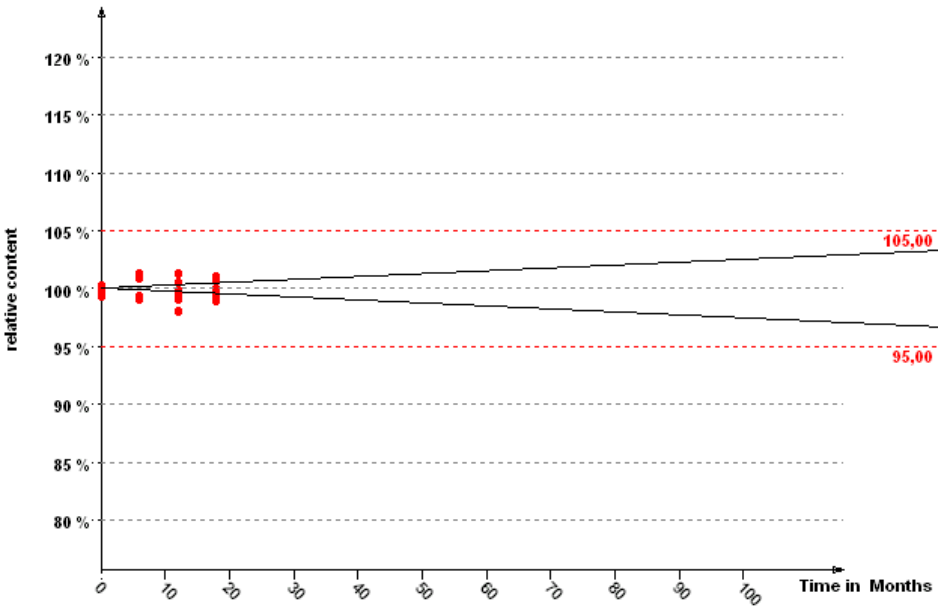
Benzo[b]fluoranthene - T=18°C



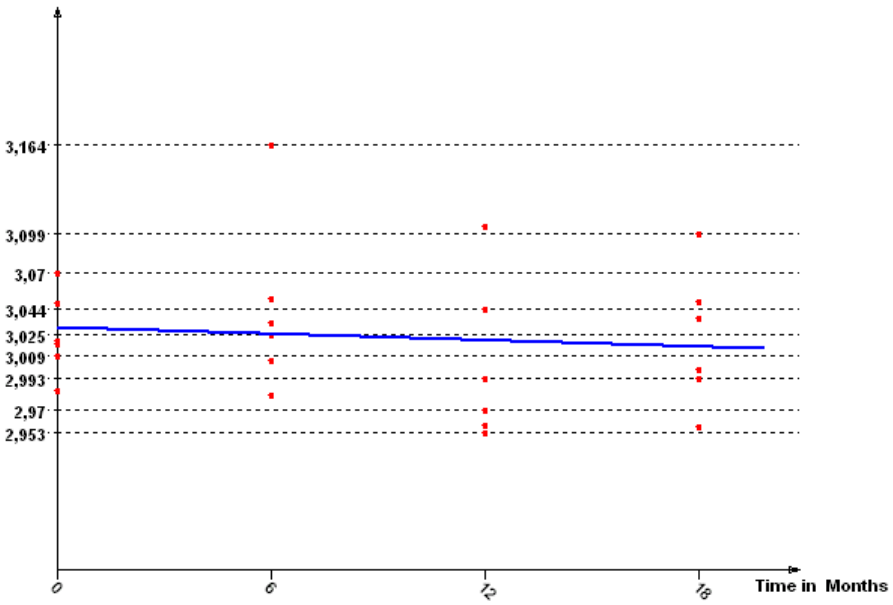
Shelf Life and Associated Ults, T=+4 °C



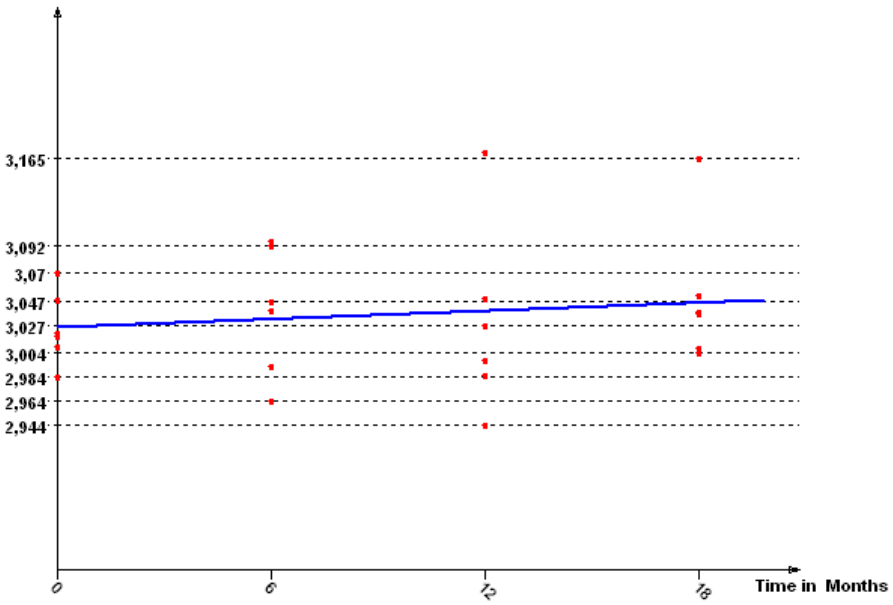
Shelf Life and Associated Ults, T=+18 °C



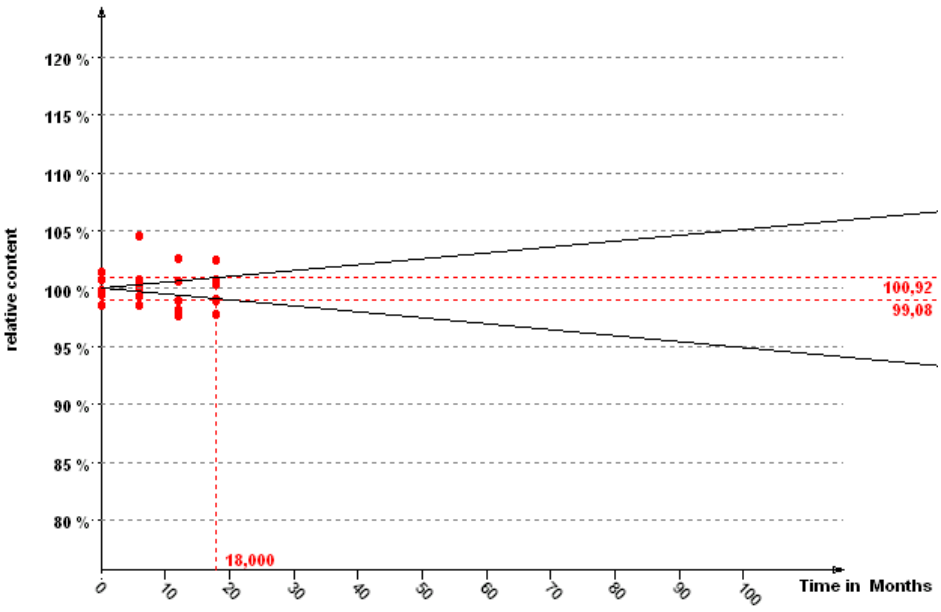
Benzo[k]fluoranthene - T=4°C



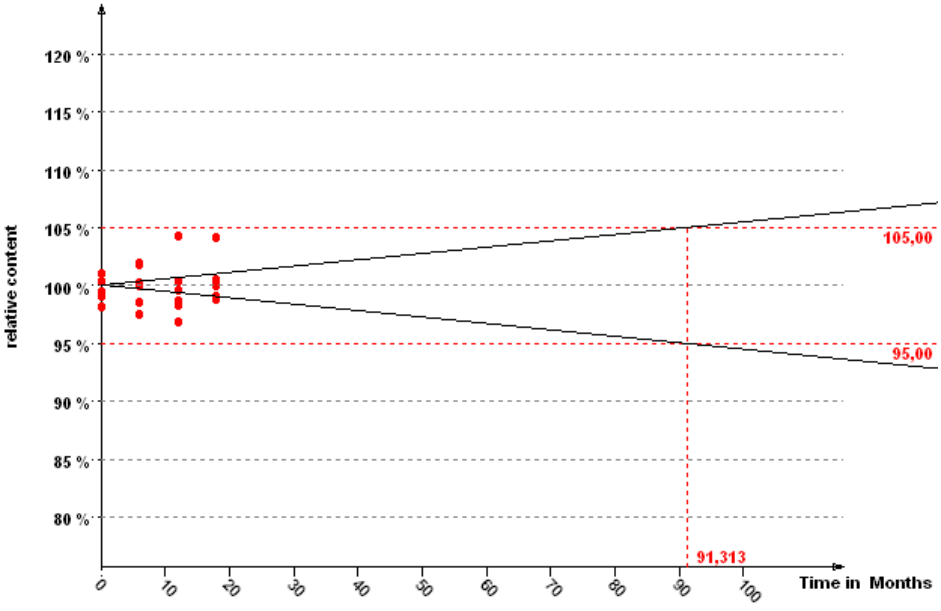
Benzo[k]fluoranthene - T=18°C



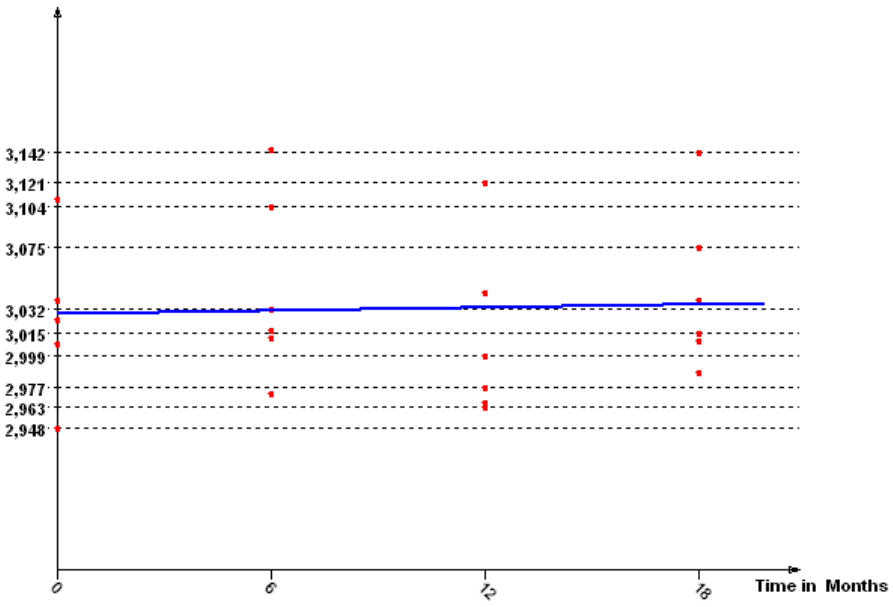
Shelf Life and Associated Ults, T=+4 °C



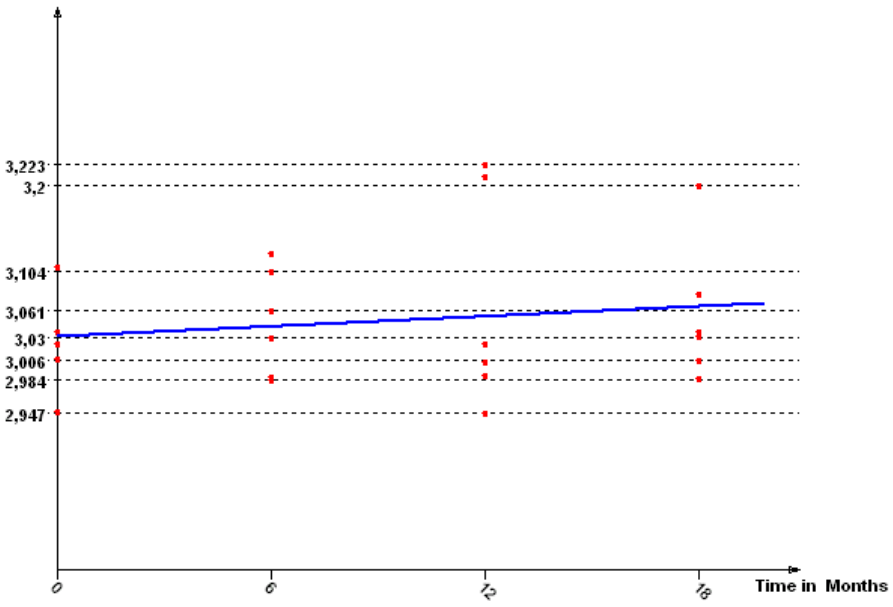
Shelf Life and Associated Ults, T=+18 °C



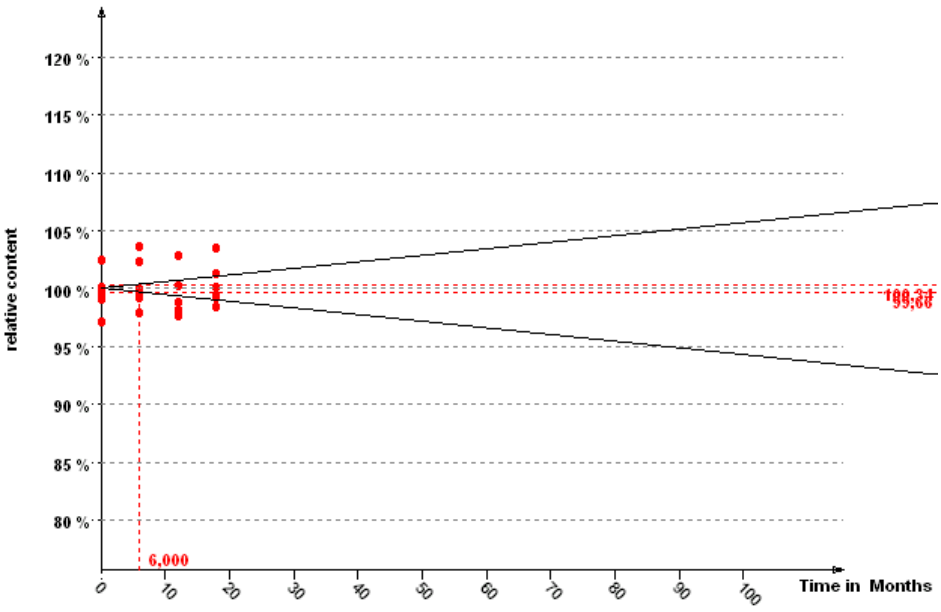
Benzo[j]fluoranthene - T=4°C



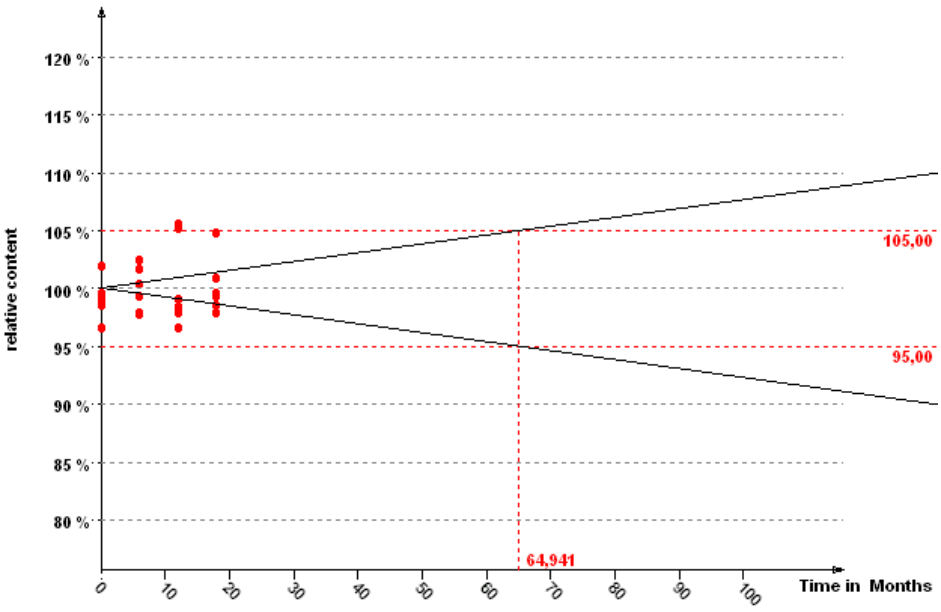
Benzo[j]fluoranthene - T=18°C



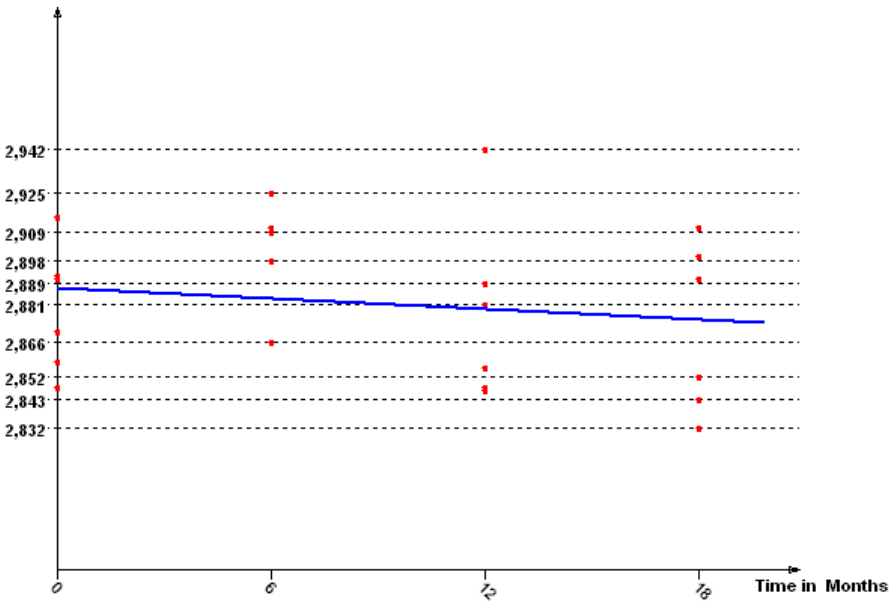
Shelf Life and Associated Ults, T=+4 °C



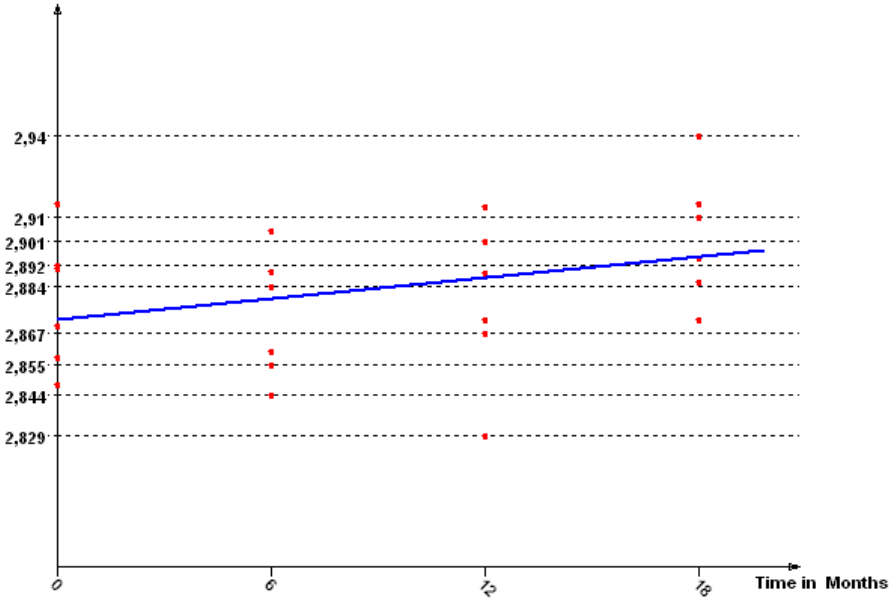
Shelf Life and Associated Ults, T=+18 °C



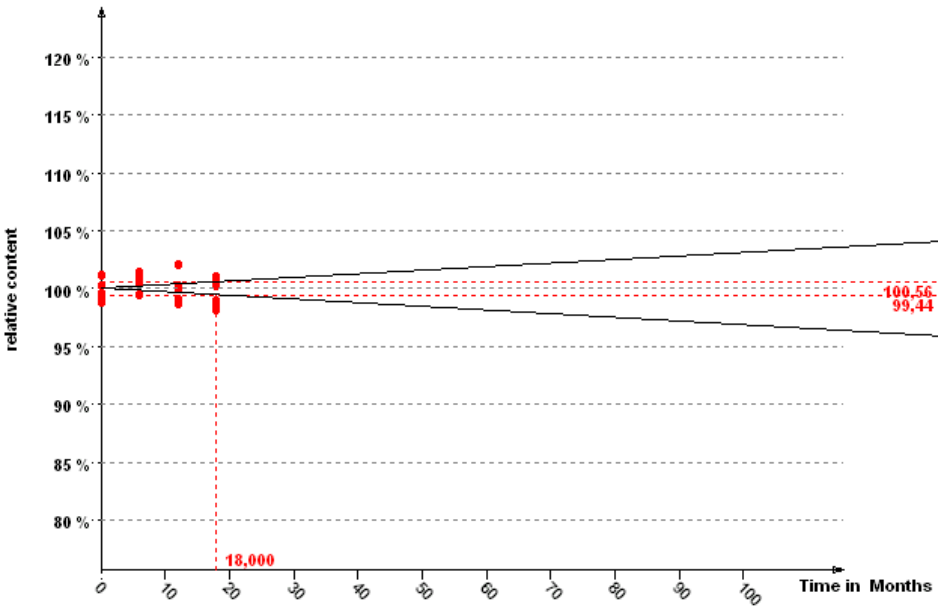
Benzo[a]pyrene - T=4°C



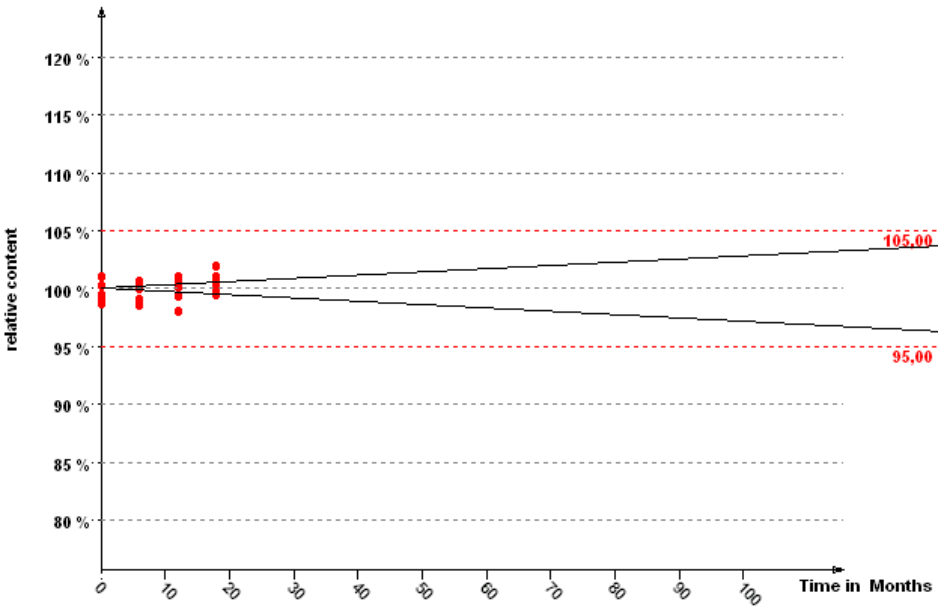
Benzo[a]pyrene - T=18°C



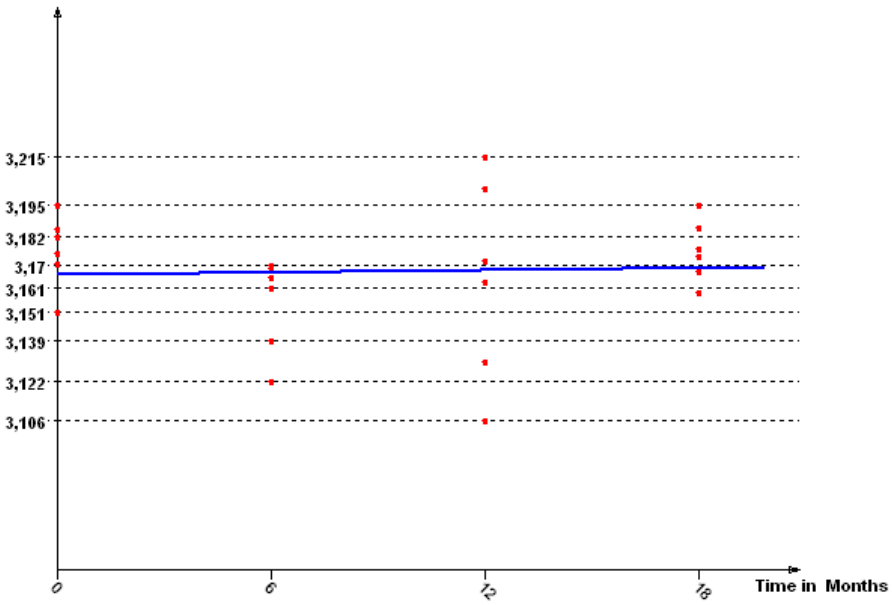
Shelf Life and Associated Ults, T=+4 °C



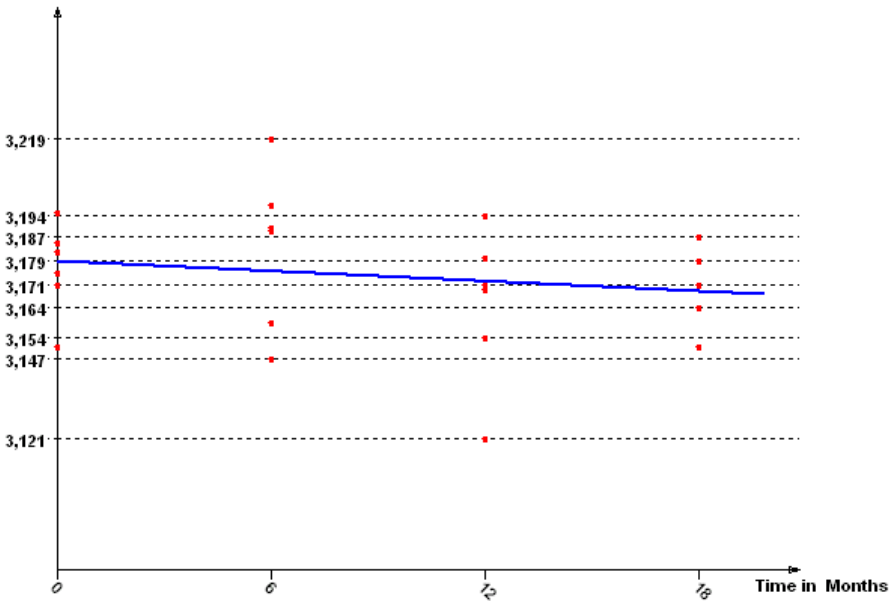
Shelf Life and Associated Ults, T=+18 °C



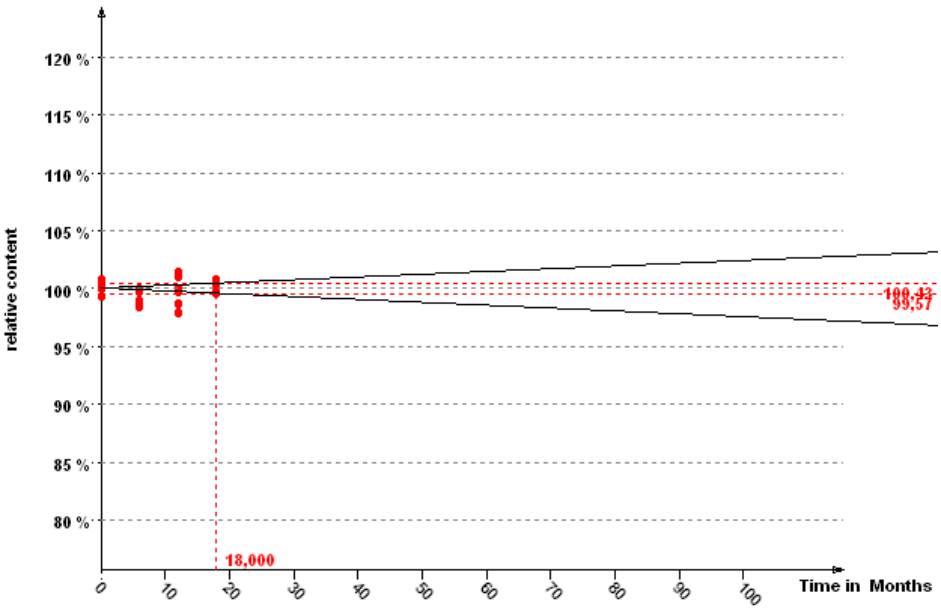
Indeno[1,2,3-cd]pyrene - T=4°C



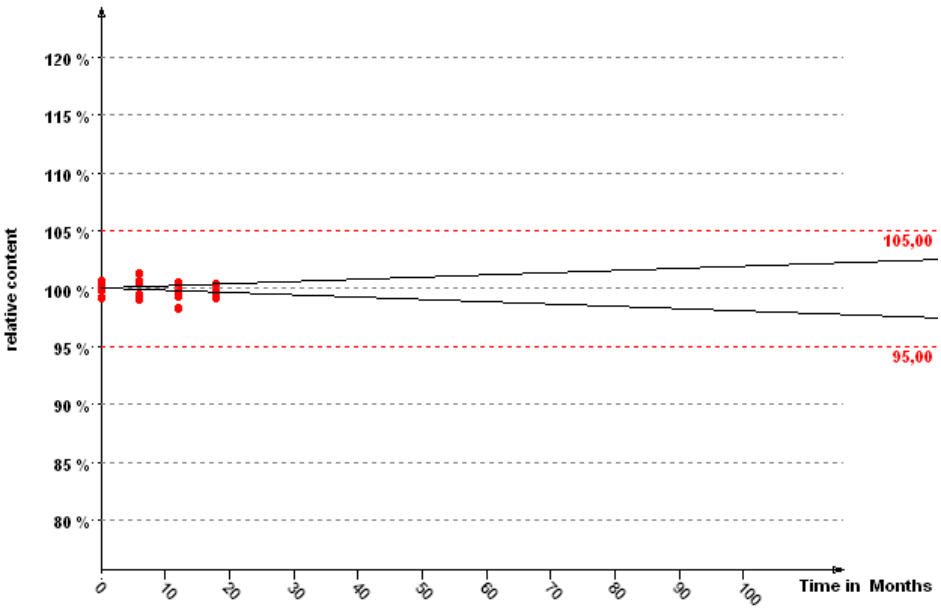
Indeno[1,2,3-cd]pyrene - T=18°C



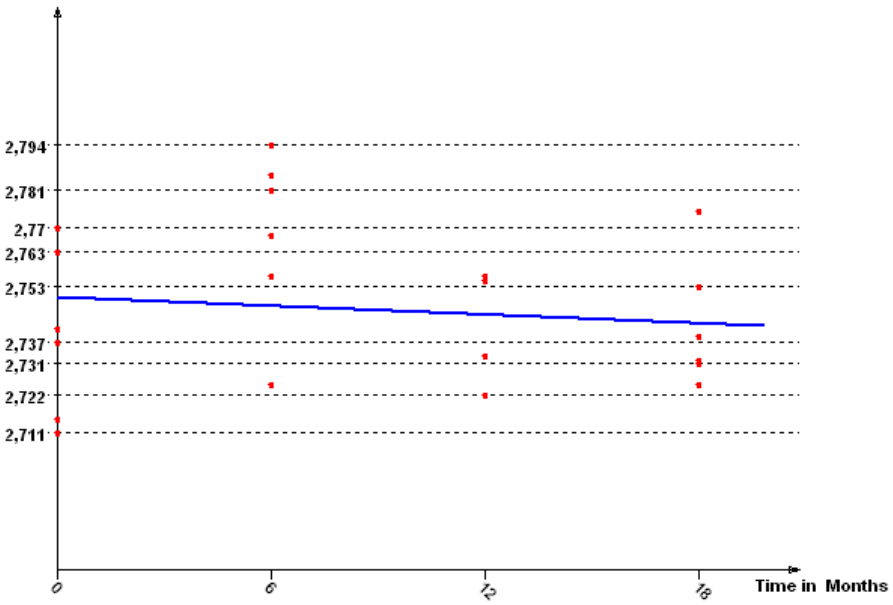
Shelf Life and Associated Ults, T=+4 °C



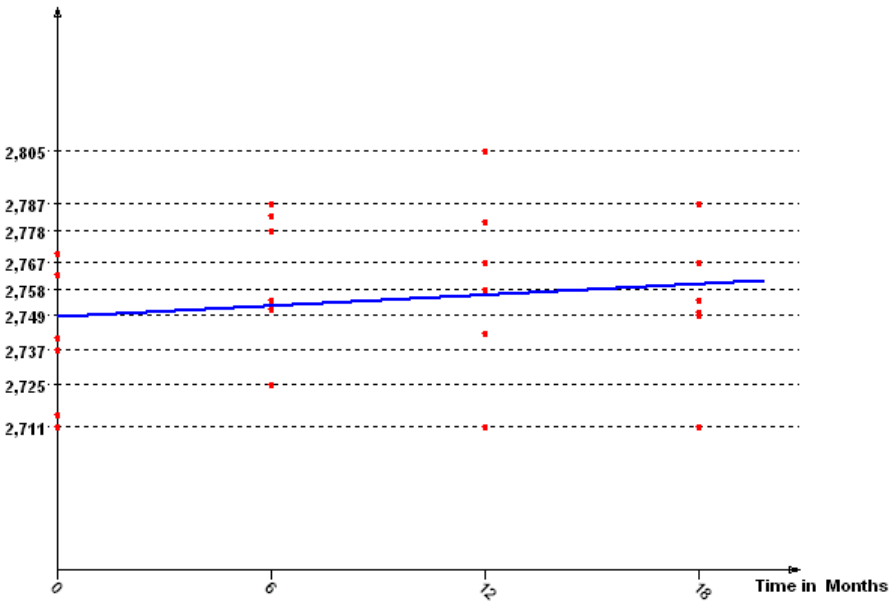
Shelf Life and Associated Ults, T=+18 °C



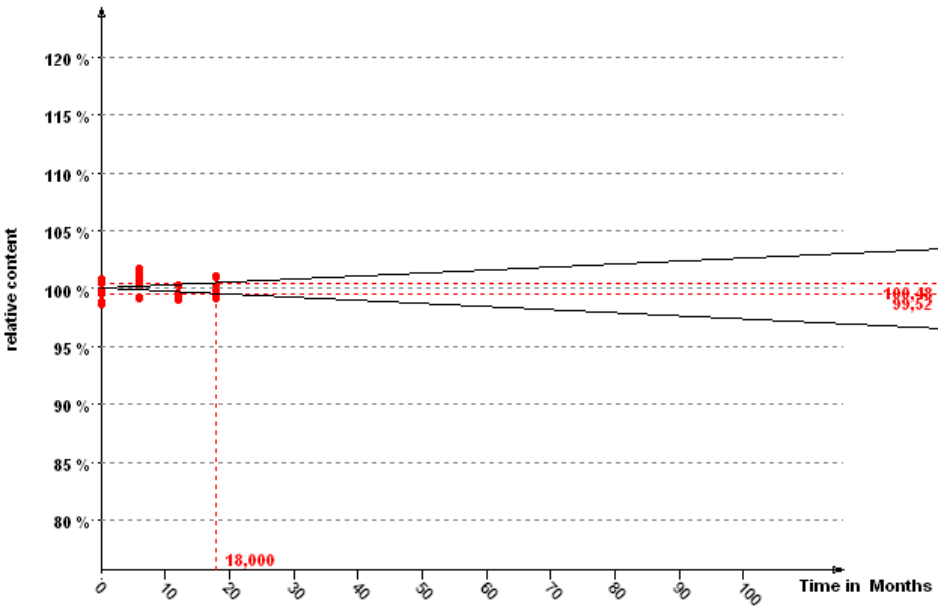
Dibenz[a,h]anthracene - T=4°C



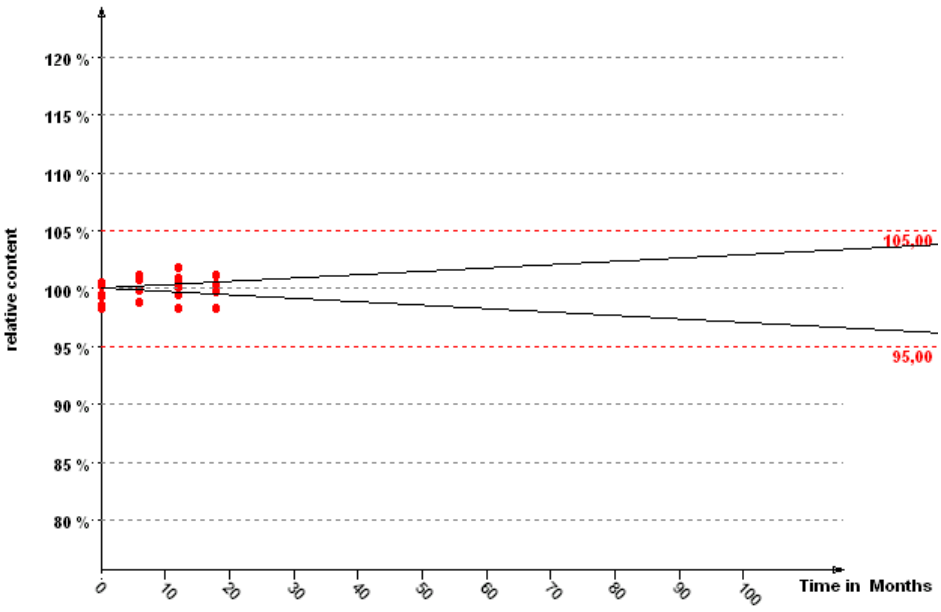
Dibenz[a,h]anthracene - T=18°C



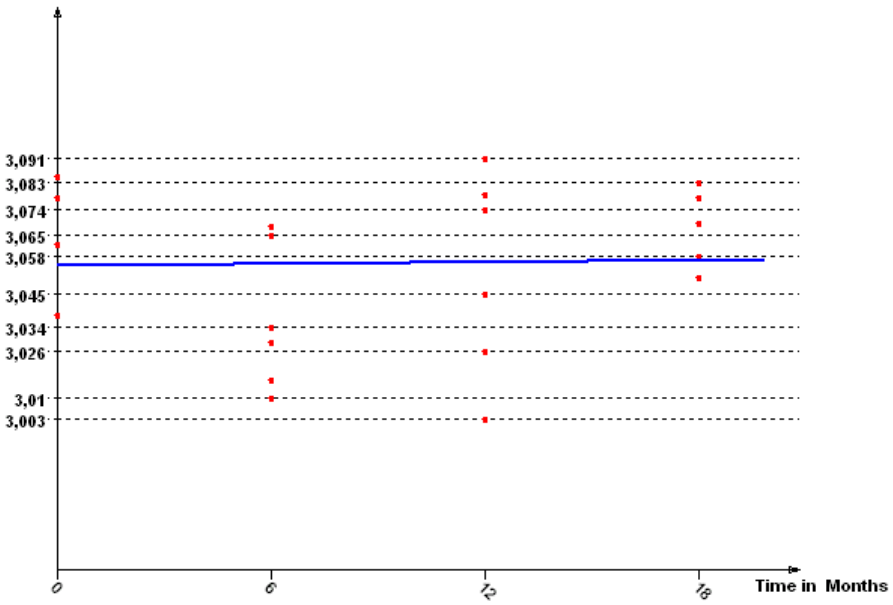
Shelf Life and Associated Ults, T=+4 °C



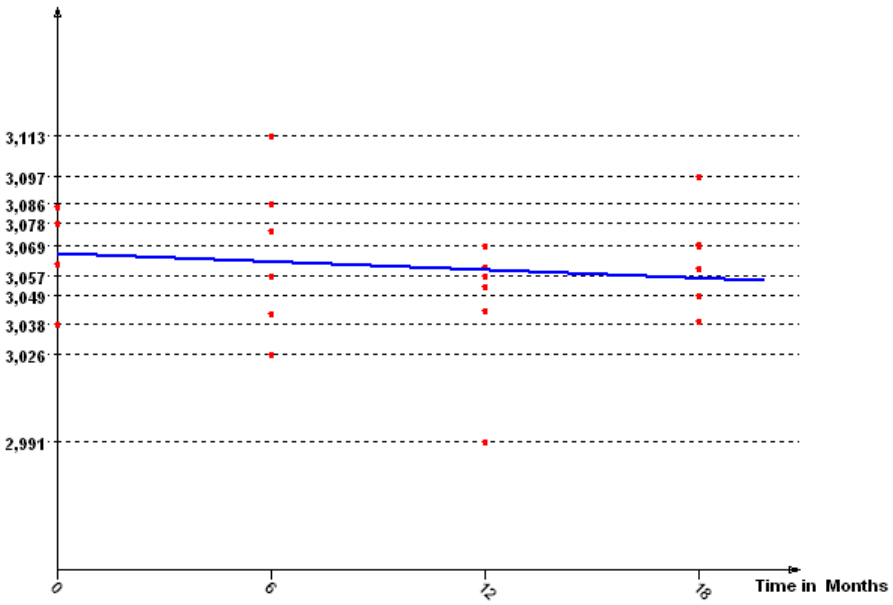
Shelf Life and Associated Ults, T=+18 °C



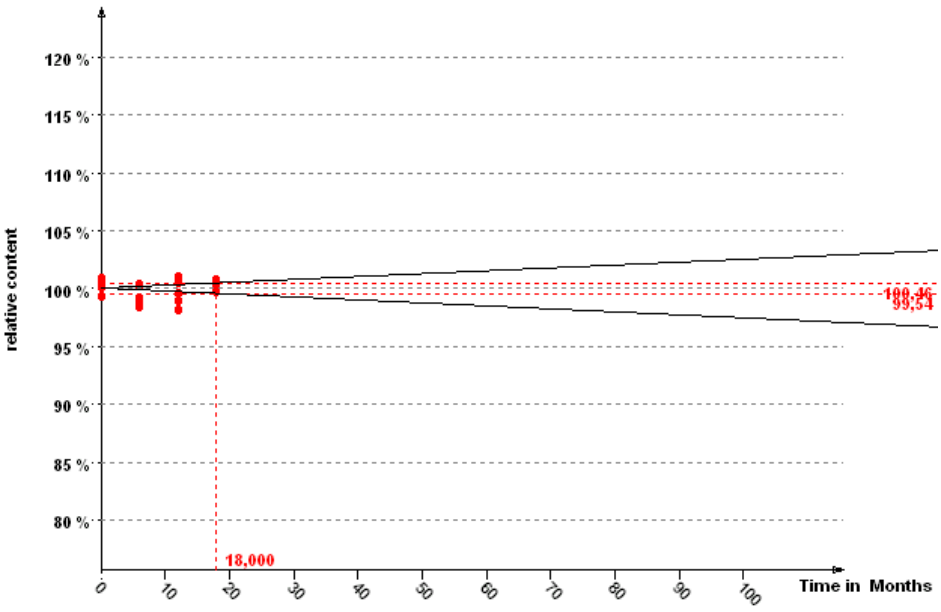
Benzo[ghi]perylene - T=4°C



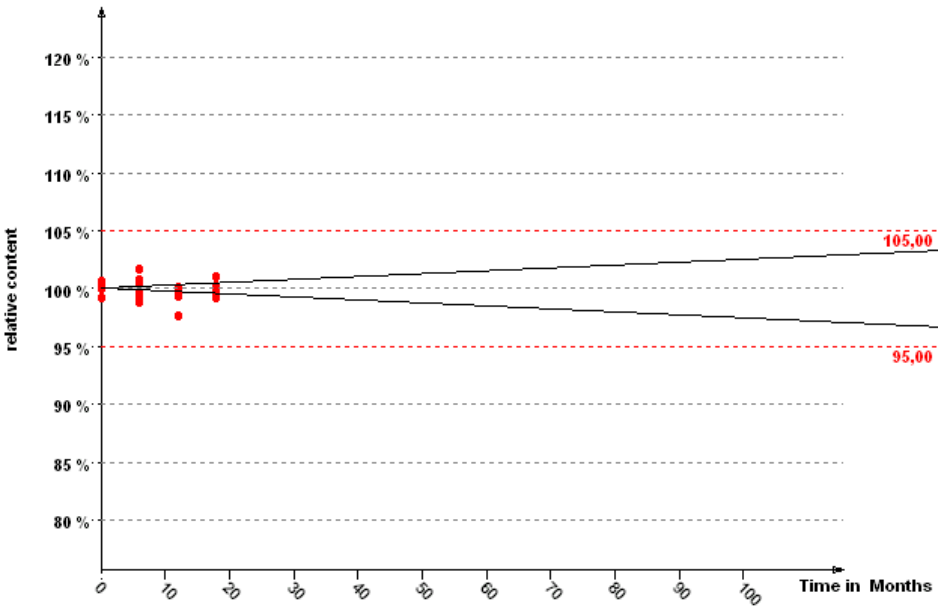
Benzo[ghi]perylene - T=18°C



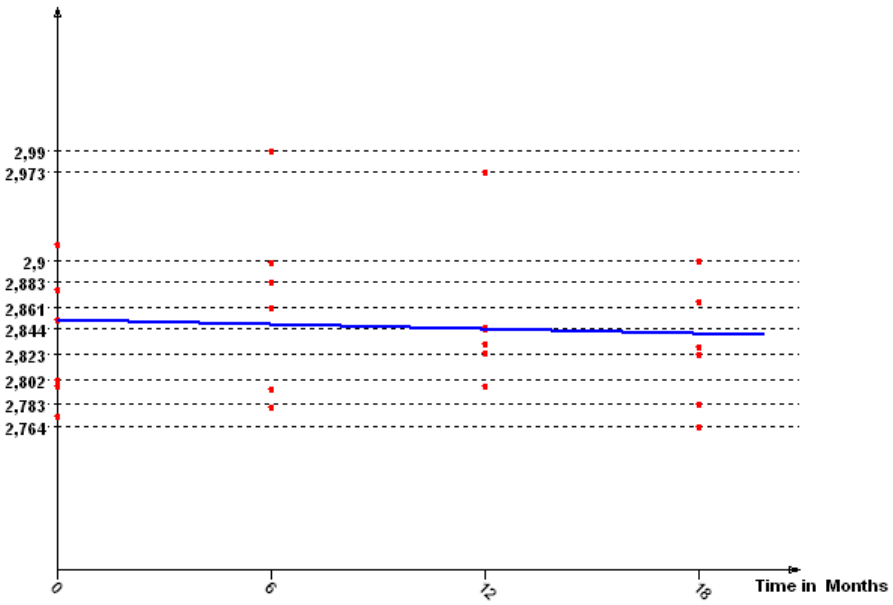
Shelf Life and Associated Ults, T=+4 °C



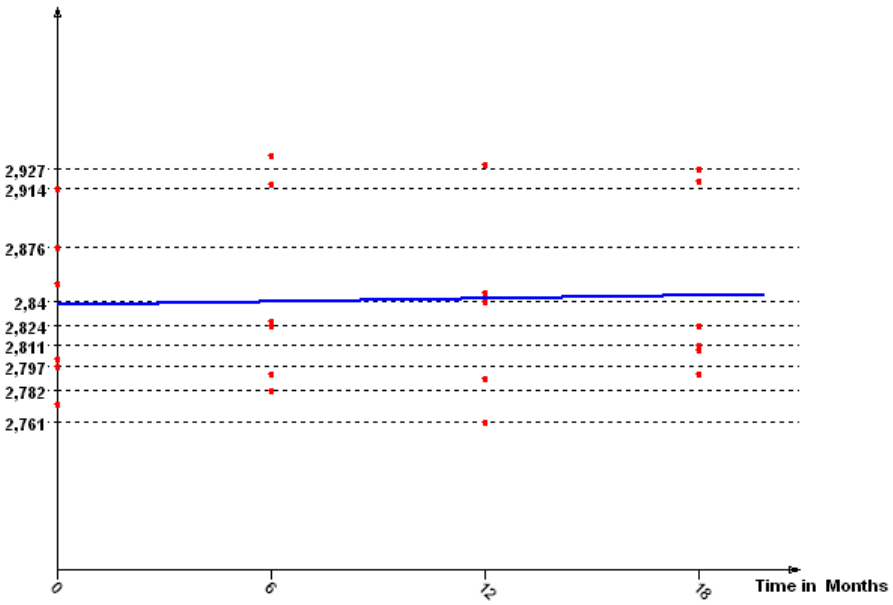
Shelf Life and Associated Ults, T=+18 °C



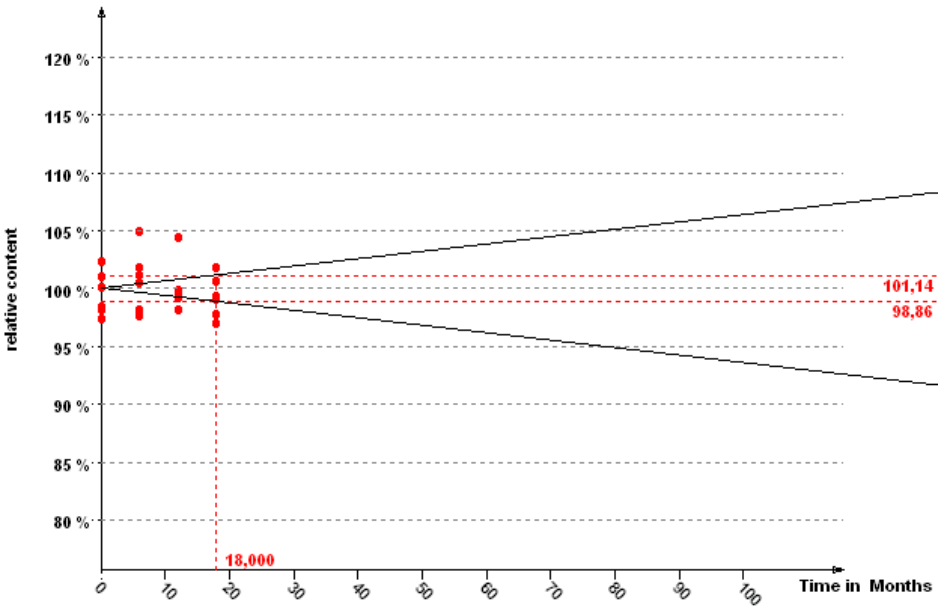
Dibenzo[a,l]pyrene - T=4°C



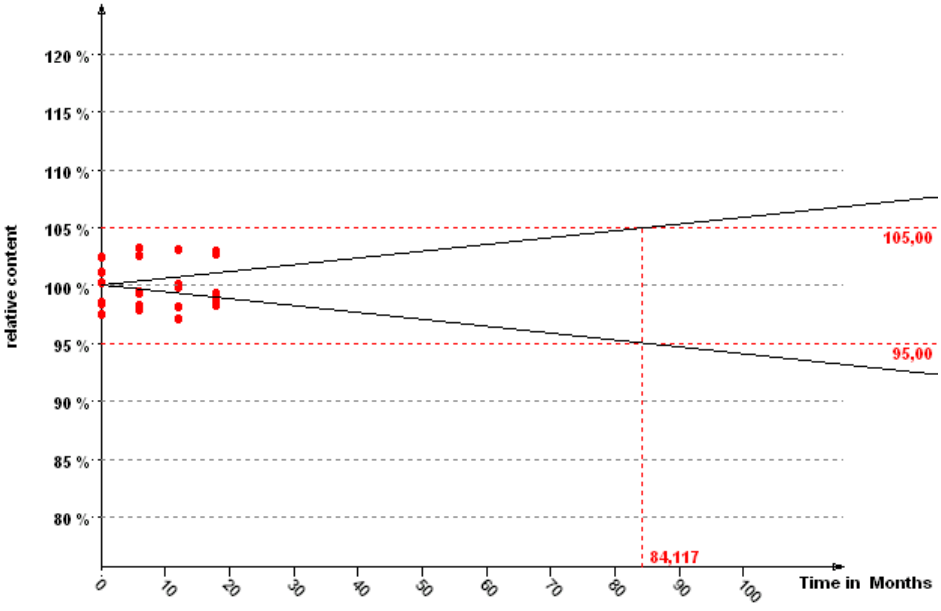
Dibenzo[a,l]pyrene - T=18°C



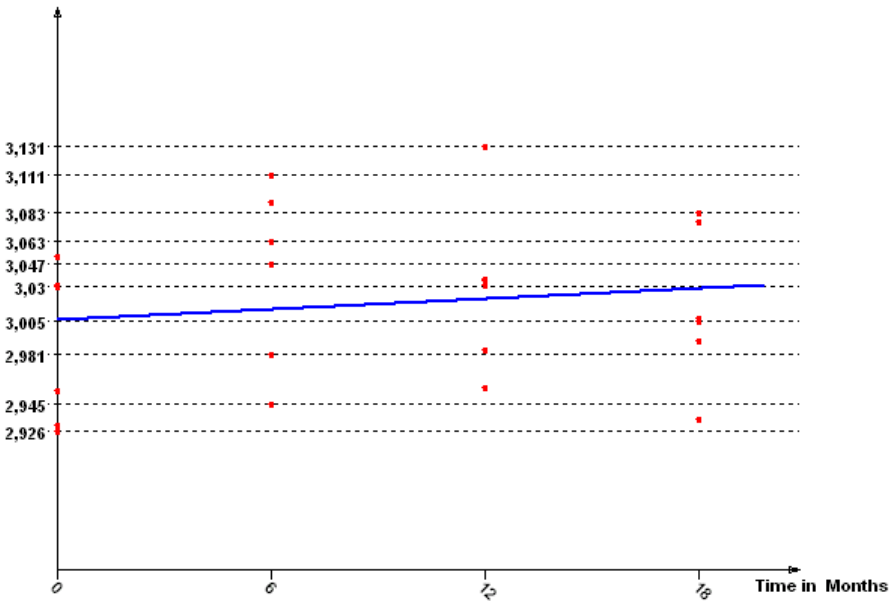
Shelf Life and Associated Ults, T=+4 °C



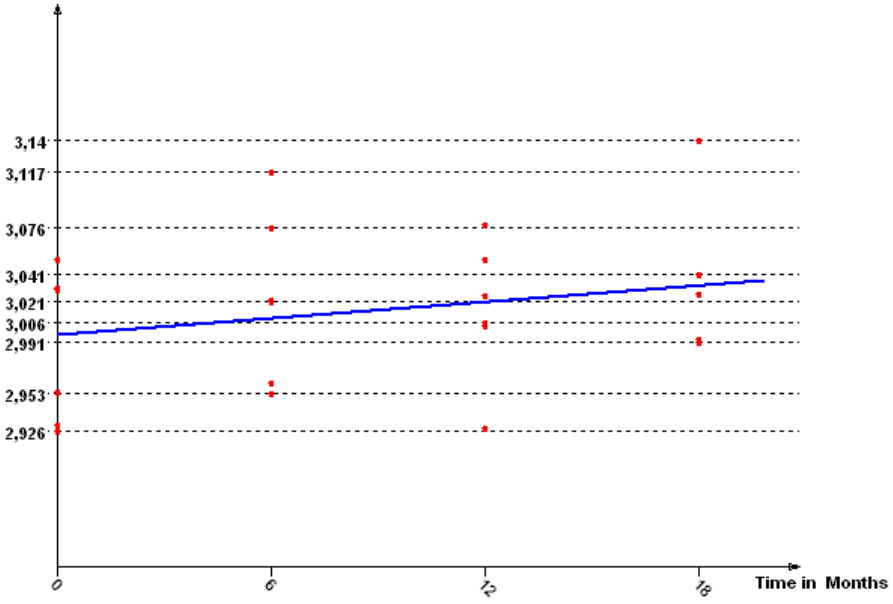
Shelf Life and Associated Ults, T=+18 °C



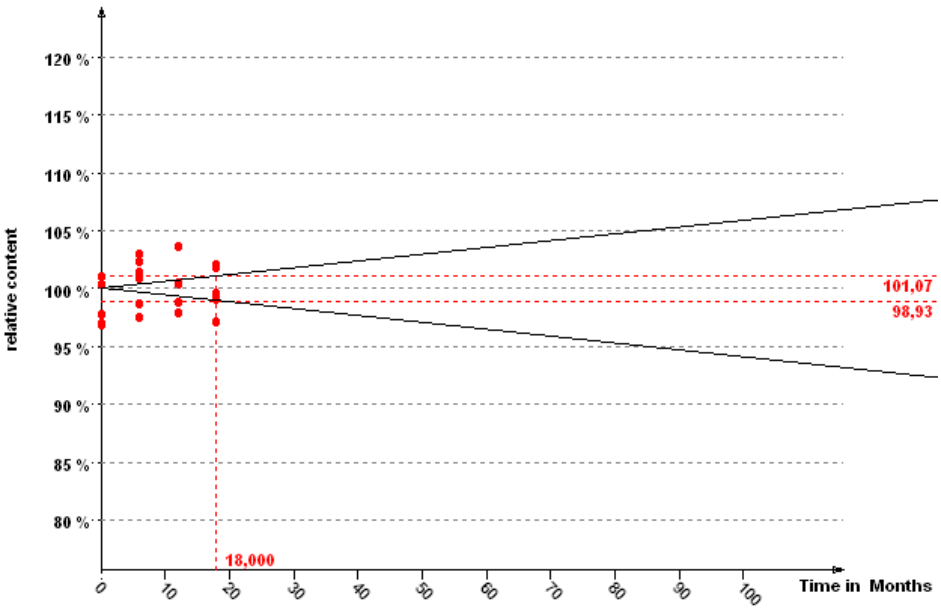
Dibenzo[a,e]pyrene - T=4°C



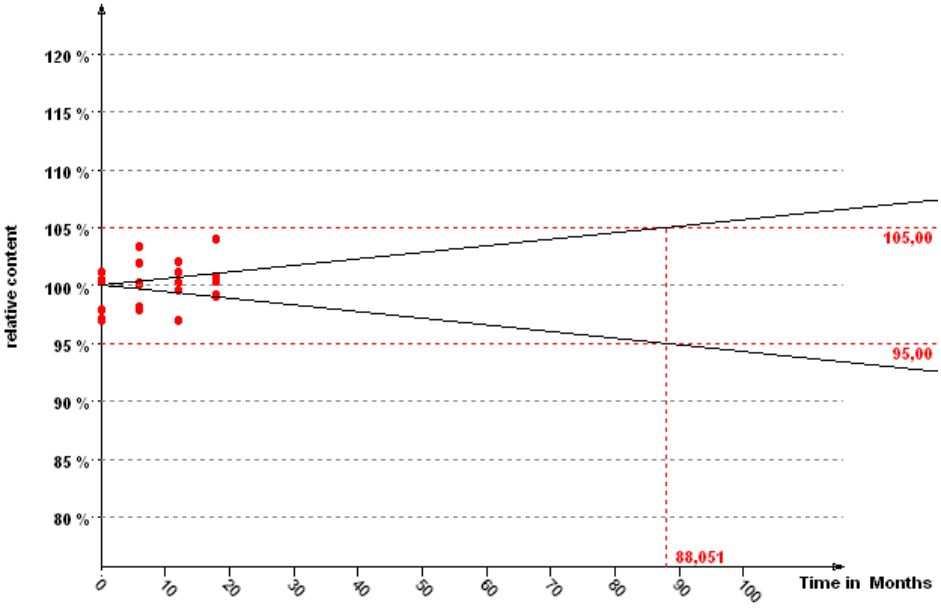
Dibenzo[a,e]pyrene - T=18°C



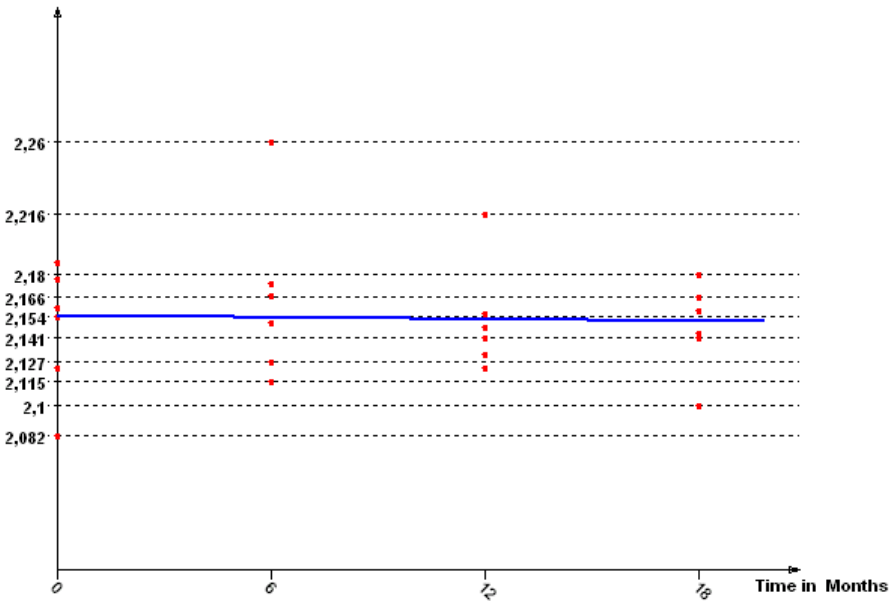
Shelf Life and Associated Ults, T=+4 °C



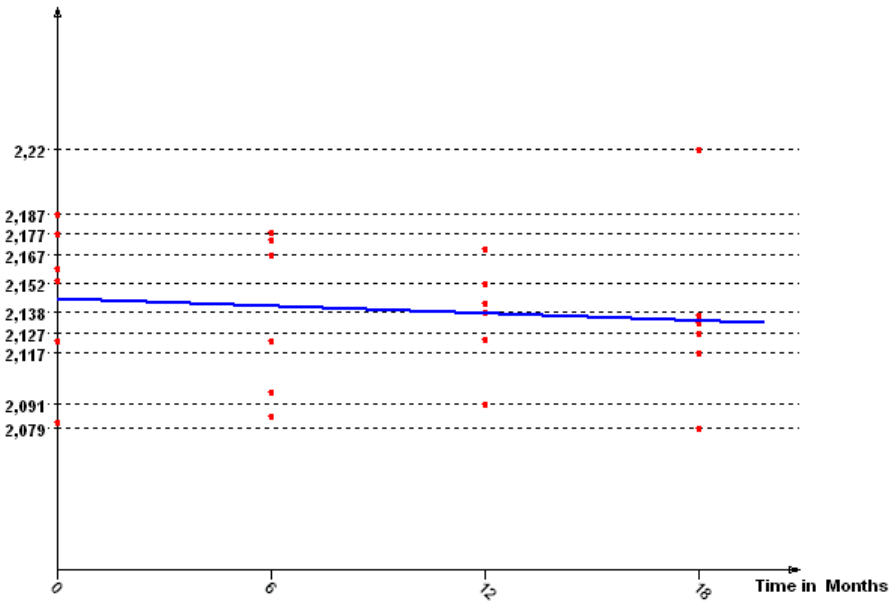
Shelf Life and Associated Ults, T=+18 °C



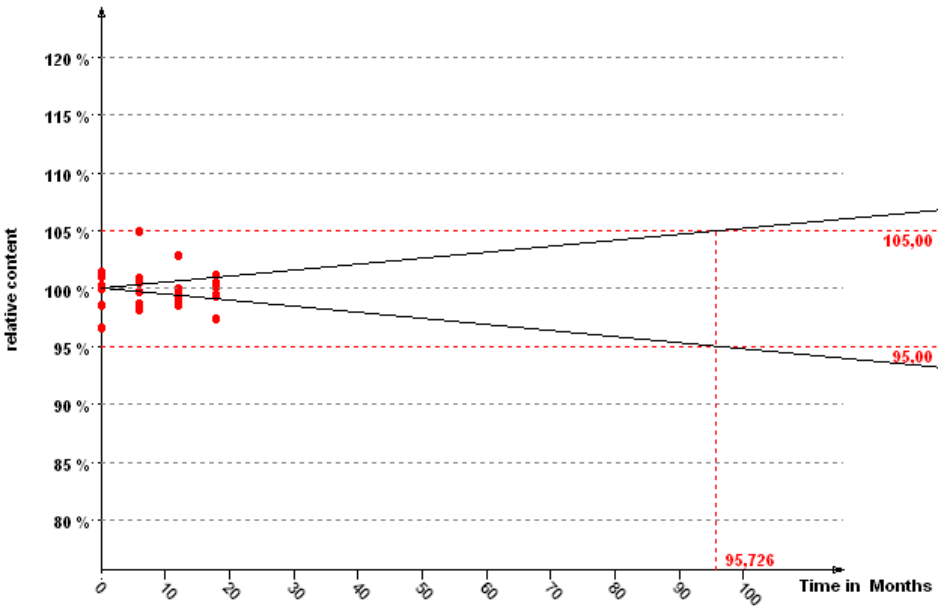
Dibenzo[a,ipyrene - T=4°C



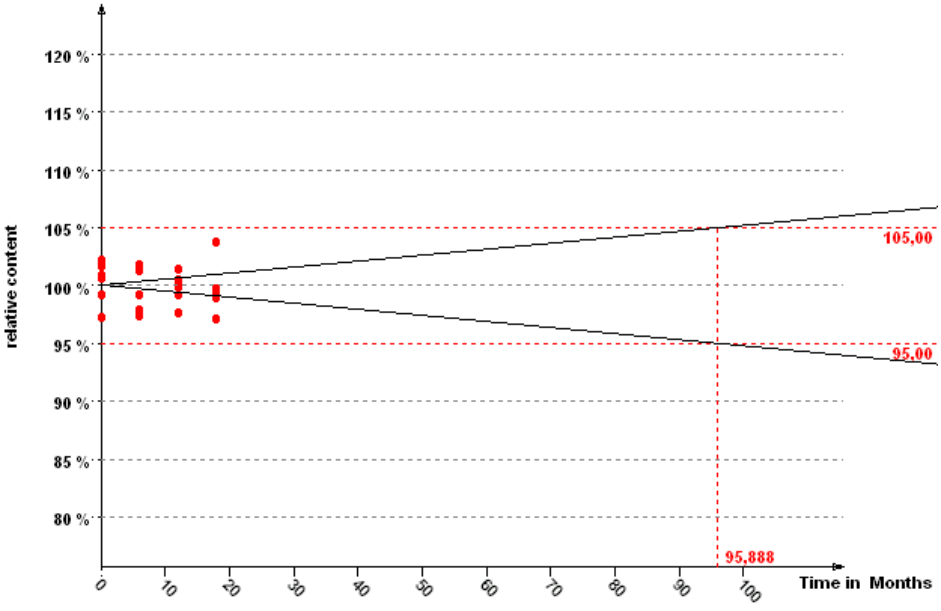
Dibenzo[a,ipyrene - T=18°C



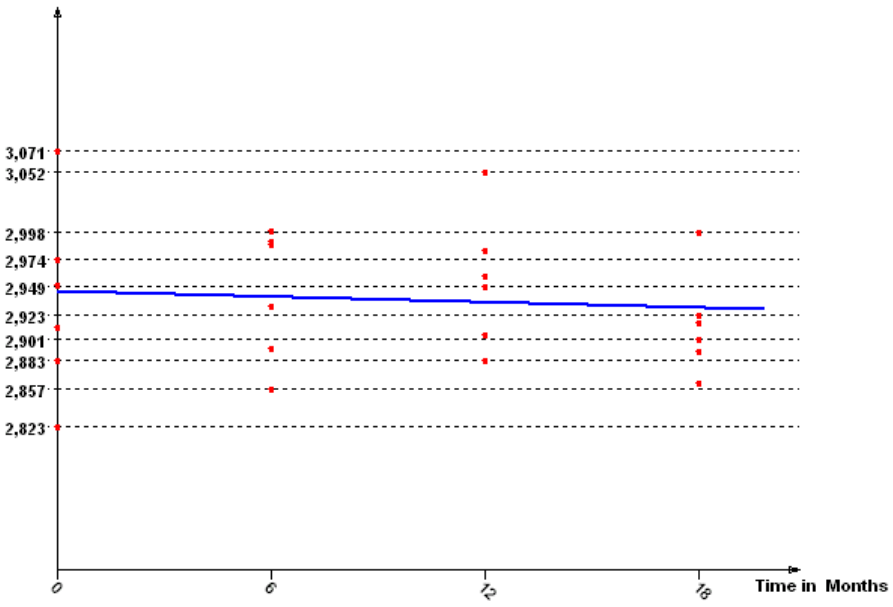
Shelf Life and Associated Ults, T=+4 °C



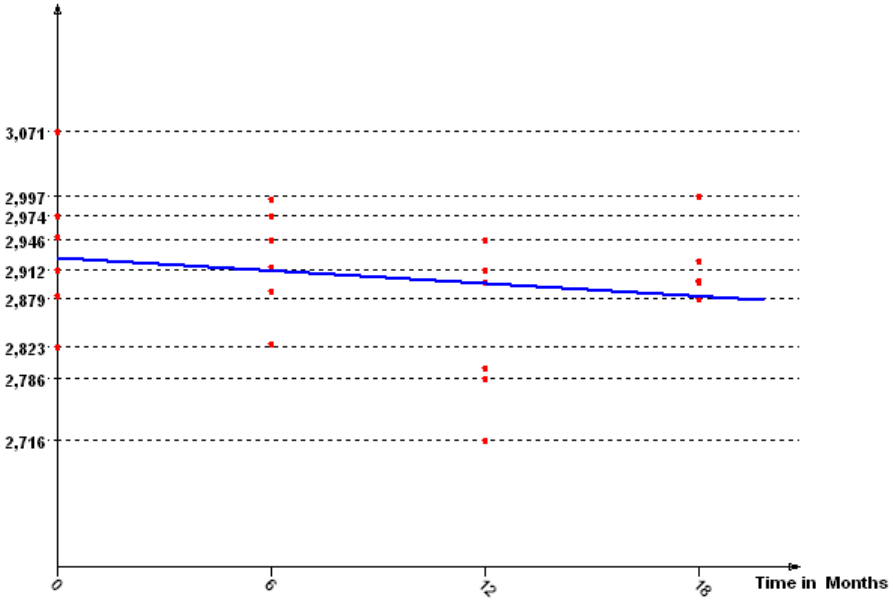
Shelf Life and Associated Ults, T=+18 °C



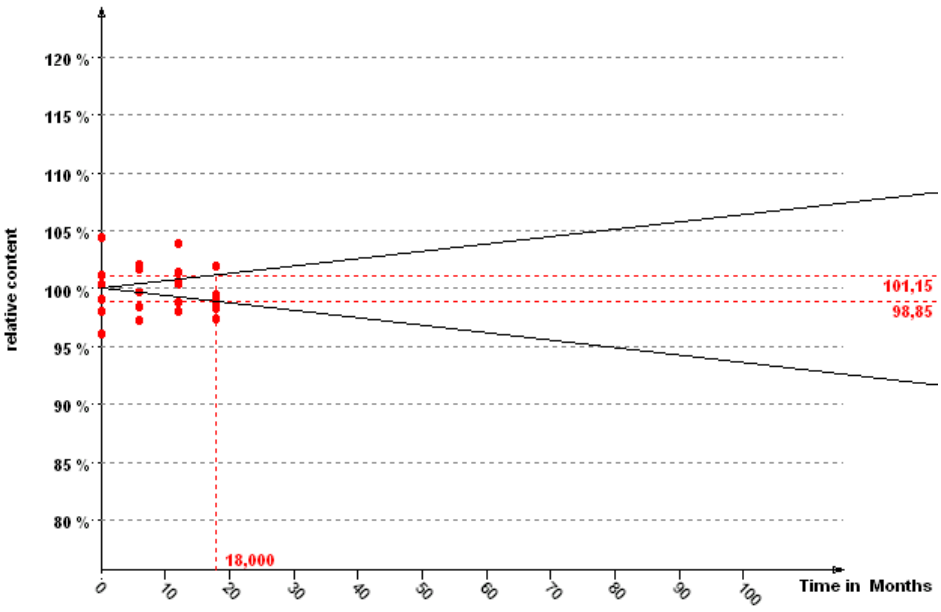
Dibenz[a,h]anthracene - T=4°C



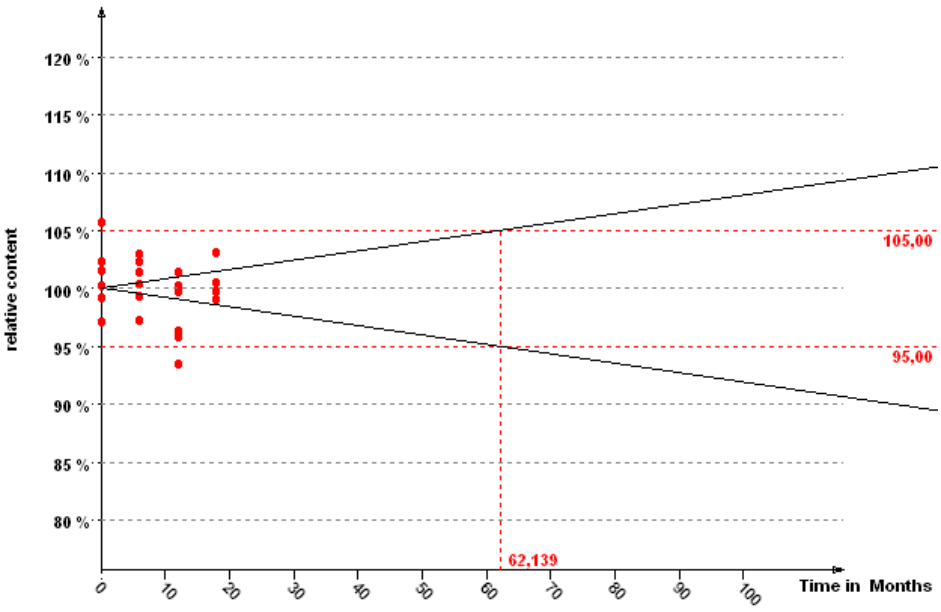
Dibenz[a,h]anthracene - T=18°C



Shelf Life and Associated Ults, T=+4 °C



Shelf Life and Associated Ults, T=+18 °C



ANNEX D. Confirmation measurement

				BENZO[*c*] FLUORENE		BENZO[*a*] ANTHRACENE		CYCLOPENTA[*cd*] PYRENE		CHRYSENE		5-METHYL CHRYSENE	
	Column	Ampoule	Calibrant	Mass fraction	*U*	Mass fraction	*U*	Mass fraction	*U*	Mass fraction	*U*	Mass fraction	*U*
				µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Gravimetric preparation/ purity				**2.13**	**0.11**	**3.09**	**0.04**	**2.96**	**0.12**	**3.06**	**0.05**	**3.08**	**0.07**
Lab 1	**DB-17MS**	**1815**	**BCR**	2.217	0.032	3.104	0.035	2.942	0.046	3.084	0.053	3.076	0.054
		86		2.224	0.031	3.108	0.034	2.950	0.051	3.098	0.051	3.086	0.050
		563		2.229	0.040	3.090	0.038	2.914	0.059	3.089	0.051	3.074	0.062
Lab 2	**DB-17HT**	**449**	**BCR**	2.246	0.12	3.112	0.07	3.030	0.02	3.085	0.06	3.102	0.13
		896		2.350	0.191	3.114	0.081	3.018	0.087	3.079	0.034	3.058	0.203
		003		2.300	0.128	3.103	0.072	3.009	0.034	3.055	0.113	3.059	0.116
Lab 2	**DB-5MS**	**449**	**BCR**	2.189	0.064	3.106	0.06	3.052	0.09	3.056	0.06	3.087	0.15
		896		2.273	0.332	3.109	0.086	3.048	0.180	3.103	0.076	3.131	0.315
		003		2.221	0.096	3.084	0.061	2.978	0.212	3.039	0.189	3.216	0.202

Lab 3 is not reported due to lack of repeatability

	Column	Ampoule	Calibrant	BENZO[*b*] FLUORANTHENE		BENZO[*k*] FLUORANTHENE		BENZO[*j*] FLUORANTHENE		BENZO[*a*] PYRENE		INDENO[1.2.3-*cd*]PYRENE	
				Mass fraction	*U*	Mass fraction	*U*	Mass fraction	*U*	Mass fraction	*U*	Mass fraction	*U*
				µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Gravimetric preparation/ purity				**3.05**	**0.05**	**3.06**	**0.08**	**3.05**	**0.10**	**2.86**	**0.07**	**3.04**	**0.05**
Lab 1	**DB-17MS**	**1815**	**BCR**	3.038	0.053	3.109	0.061	3.083	0.064	2.919	0.028	3.116	0.040
		86		3.051	0.048	3.078	0.039	3.045	0.039	2.895	0.034	3.107	0.042
		563		3.035	0.045	3.035	0.047	3.014	0.047	2.877	0.046	3.087	0.035
Lab 2	**DB-17HT**	**449**	**BCR**	3.052	0.07	3.049	0.06	3.039	0.13	2.864	0.07	3.045	0.06
		896		3.036	0.082	3.066	0.053	3.044	0.076	2.823	0.083	3.059	0.064
		003		3.033	0.064	3.032	0.037	3.019	0.050	2.842	0.067	3.035	0.054
Lab 2	**DB-5MS**	**449**	**BCR**			3.025	0.12			2.894	0.08	3.040	0.06
		896		1)		3.122	0.183	1)		2.897	0.088	3.050	0.138
		003				3.036	0.106			2.816	0.165	3.088	0.101

1) Benzo[*b*]fluroanthene and Benzo[*j*]fluoranthene are not separated on this column.

Lab 3 is not reported due to lack of repeatability

				DIBENZO[a.h] ANTHRACENE		BENZO[*g.h.*i] PERYLENE		DIBENZO[*a.l*] PYRENE		DIBENZO[*a.e*] PYRENE		DIBENZO[*a.i*] PYRENE	
	Column	Ampoule	Calibrant	Mass fraction	*U*	Mass fraction	*U*	Mass fraction	*U*	Mass fraction	*U*	Mass fraction	*U*
				µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Gravimetric preparation/ purity				**2.76**	**0.05**	**3.07**	**0.05**	**2.85**	**0.10**	**2.97**	**0.10**	**2.37**	**0.15**
Lab 1	**DB-17MS**	**1815**	**BCR**	2.763	0.053	3.101	0.031	2.847	0.067	2.921	0.070	2.162	0.147
		86		2.800	0.057	3.093	0.031	2.898	0.049	2.975	0.056	2.195	0.151
		563		2.751	0.063	3.089	0.039	2.874	0.050	2.986	0.045	2.159	0.146
Lab 2	**DB-17HT**	**449**	**BCR**	2.784	0.08	3.077	0.06	2.821	0.18	2.947	0.10	2.331	0.11
		896		2.762	0.066	3.093	0.078	2.849	0.085	2.924	0.112	2.309	0.079
		003		2.747	0.060	3.065	0.122	2.890	0.211	2.991	0.194	2.332	0.151
Lab 2	**DB-5MS**	**449**	**BCR**	2.762	0.02	3.101	0.06	2.795	0.05	2.948	0.06	2.343	0.09
		896		2.803	0.205	3.091	0.085	2.992	0.564	2.971	0.114	2.379	0.068
		003		2.779	0.057	3.069	0.114	2.930	0.416	3.037	0.122	2.330	0.101

Lab 3 is not reported due to lack of repeatability

European Commission

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Abstract

This report describes the preparation of a calibration solution of polycyclic aromatic hydrocarbons (PAHs) (ERM-AC213) containing benzo[*a*]pyrene, benz[*a*]anthracene, cyclopenta[*cd*]pyrene, chrysene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, dibenz[*a*,*h*]anthracene, dibenzo[*a*,*l*]pyrene, dibenzo[*a*,*e*]pyrene, dibenzo[*a*,*i*]pyrene, indeno[1,2,3-*cd*]pyrene, 5-methylchrysene and benzo[*c*]fluorene and the certification of their content (mass fraction) in the solution.

The preparation of the calibrant, homogeneity and stability studies and confirmation measurements with a discussion of the results are described hereafter. Uncertainties were calculated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [1] and include uncertainties due to the processing, purity assessment and possible instability.

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