# Results of Proficiency Test
# PAH in Tattoo Ink
# October 2018


Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

Authors: ing. R.J. Starink
Correctors: ing. A.S. Noordman-de Neef & ing. G.A. Oosterlaken-Buijs


Report: iis18H01

January 2019

**CONTENTS**

# 1 INTRODUCTION

In the past years, tattoos have become very popular worldwide, and millions of people have tattoos with mainly black colours. Black tattoo inks are usually based on soot, are not regulated and may contain hazardous polycyclic aromatic hydrocarbons (PAH).
Therefore in 2008 a committee of ministers in the EU adopted a resolution (ResAP(2008)1) on requirements and criteria for the safety of tattoos. In resolution ResAP(2008)1 on table 3 is mentioned that the maximum allowed concentration for PAH into tattoo ink is 0.5 mg/kg, except for Benzo[a]pyrene which is 5 µg/kg.
No reference materials (RMs) for PAH in tattoo ink are available to optimise the determination of PAH. As an alternative, participation in a proficiency test may enable the laboratories to check their performance and thus to increase this comparability.

On request of a number of laboratories, the Institute for Interlaboratory Studies (iis) decided to set up a new proficiency test of the determination of PAH in Tattoo Ink during the annual testing program 2018/2019.
In this interlaboratory study 9 laboratories from 8 different countries registered for participation. See appendix 3 for the number of participants per country. In this report, the results of the 2018 proficiency test are presented and discussed. This report is also electronically available through the iis website ww.iisnl.com.

# 2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organiser of this proficiency test (PT). Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC 17025 accredited laboratory. It was decided to send 2 different samples of tattoo ink (labelled #18625 and #18626, 5ml each), both positive on PAH. The participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for statistical evaluation.

## 2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO/IEC 17043:2010. This ensures strict adherence to protocols for sample preparation and statistical evaluation and 100% confidentiality of participant's data. Feedback from the participants on the reported data is encouraged and customer's satisfaction is measured on a regular basis by sending out questionnaires.

## 2.2 PROTOCOL

The protocol followed in the organisation of this proficiency test was the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5). This protocol is electronically available through the iis website www.iisnl.com, from the FAQ page.

## 2.3 CONFIDENTIALITY STATEMENT

All data presented in this report must be regarded as confidential and for use by the participating companies only. Disclosure of the information in this report is only allowed by means of the entire report. Use of the contents of this report for third parties is only allowed by written permission of the Institute for Interlaboratory Studies. Disclosure of the identity of one or more of the participating companies will be done only after receipt of a written agreement of the companies involved.

## 2.4 SAMPLES

The first batch of black Tattoo Ink (positive on a number of PAH) was obtained from the local market. Subsamples of approx. 5 ml (in a 8 ml vial) each were prepared and labelled #18625. Seven stratified randomly selected subsamples were tested according AfPS GS2014 to check the homogeneity of the batch.

| | *Naphthalene in mg/kg* | *Acenaphthylene in mg/kg* | *Fluoranthene in mg/kg* | *Pyrene in mg/kg* |
|---|---|---|---|---|
| Sample #18625-1 | 1.88 | 2.88 | 1.22 | 14.07 |
| Sample #18625-2 | 1.90 | 3.02 | 1.31 | 14.49 |
| Sample #18625-3 | 1.93 | 3.13 | 1.32 | 14.73 |
| Sample #18625-4 | 1.92 | 3.16 | 1.34 | 15.07 |
| Sample #18625-5 | 1.93 | 3.08 | 1.31 | 14.94 |
| Sample #18625-6 | 1.86 | 2.99 | 1.32 | 14.59 |
| Sample #18625-7 | 1.94 | 3.10 | 1.30 | 15.23 |

Table 1: homogeneity test results of subsamples #18625

From the test results of table 1, the repeatabilities were calculated and compared with 0.3 times the corresponding estimated target reproducibility in agreement with the procedure of ISO 13528, Annex B2 in the next table:

| | *Naphthalene in mg/kg* | *Acenaphthylene in mg/kg* | *Fluoranthene in mg/kg* | *Pyrene in mg/kg* |
|---|---|---|---|---|
| r (observed) | 0.08 | 0.27 | 0.11 | 1.10 |
| reference method | Horwitz | Horwitz | Horwitz | Horwitz |
| 0.3 x R (ref. method) | 0.23 | 0.35 | 0.17 | 1.32 |

Table 2: evaluation of the repeatabilities of subsamples #18625

The calculated repeatabilities of the test results were in agreement with 0.3 times the corresponding estimated reproducibility using the Horwitz equation. Therefore, homogeneity of the subsamples was assumed.

The second batch of black Tattoo Ink (positive on a number of PAH) was also obtained from the local market. Subsamples of approx. 5 ml (in a 8 ml vial) each were prepared and labelled #18626. Eight stratified randomly selected subsamples were tested according AfPS GS2014 to check the homogeneity of the batch.

| | *Naphthalene in mg/kg* |
|---|---|
| Sample #18626-1 | 10.51 |
| Sample #18626-2 | 9.54 |
| Sample #18626-3 | 10.00 |
| Sample #18626-4 | 9.89 |
| Sample #18626-5 | 10.12 |
| Sample #18626-6 | 10.16 |
| Sample #18626-7 | 10.11 |
| Sample #18626-8 | 9.62 |

Table 3: homogeneity test results of subsamples #18626

From the test results of table 3, the repeatability was calculated and compared with 0.3 times the corresponding estimated target reproducibility in agreement with the procedure of ISO 13528, Annex B2 in the next table:

| | *Naphthalene in mg/kg* |
|---|---|
| r (observed) | 0.87 |
| reference method | Horwitz |
| 0.3 x R (ref. method) | 0.95 |

Table 4: evaluation of the repeatability of subsamples #18626

The calculated repeatability of the test results was in agreement with 0.3 times the corresponding estimated reproducibility using the Horwitz equation. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one sample, labelled #18625 and one sample, labelled #18626, were sent on September 19, 2018.

## 2.5 ANALYSES

The participants were asked to determine on samples #18625 and #18626 the concentrations of any of the following PAHs (CAS No. between brackets):

- Total PAH
- Naphthalene (91-20-3)
- Acenaphthylene (208-96-8)
- Acenaphthene (83-32-9)
- Fluorene (86-73-7)
- Phenanthrene (85-01-8)
- Anthracene (120-12-7)
- Fluoranthene (206-44-0)
- Pyrene (129-00-0)
- Benzo[a]anthracene (56-55-3)
- Chrysene (218-01-9)
- Triphenylene (217-59-4)
- Sum of Chrysene and Triphenylene
- Benzo[b]fluoranthene (205-99-2)
- Benzo[j]fluoranthene (205-82-3)
- Benzo[k]fluoranthene (207-08-9)
- Sum of [b],[j] and [k] Benzofluoranthenes
- Benzo[e]pyrene (192-97-2)
- Benzo[a]pyrene (50-32-8)
- Indeno[1,2,3-c,d]pyrene (193-39-5)
- Dibenzo[a,h]anthracene (53-70-3)
- Benzo[g,h,i]perylene (191-24-2)
- Cyclopenta[c,d]pyrene (27208-37-3)

It was explicitly requested to treat the samples as if they were routine samples and to report the test results using the indicated units on the report form and not to round the test results, but to report as much significant figures as possible. It was also requested not to report “less than’ results, which are above the detection limit, because such results cannot be used for meaningful statistical evaluations.

To get comparable test results a detailed report form and a letter of instructions are prepared. On the report form the reporting units are given as well as the appropriate reference test methods that will be used during the evaluation. The detailed report form and the letter of instructions are both made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The participating laboratories were also requested to confirm sample receipt on this data entry portal. The letter of instructions can also be downloaded from the iis website www.iisnl.com.

## 3 RESULTS

During five weeks after sample dispatch, the test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The reported test results are tabulated per sample and determination in appendix 1 of this report. The laboratories are presented by the code numbers.

Directly after the deadline, a reminder was sent to those laboratories that had not reported test results at that moment.
Shortly after the deadline, the available test results were screened for suspect data. A test result was called suspect in case the Huber Elimination Rule (a robust outlier test) found it to be an outlier. The laboratories that produced these suspect data were asked to check the reported test results (no reanalyses). Additional or corrected test results are used for the data analysis and the original results are placed under 'Remarks' in the result tables in appendix 1. Test results that came in after the deadline were not taken into account in this screening for suspect data and thus these participants were not requested for checks.

### 3.1 STATISTICS

The protocol followed in the organisation of this proficiency test wast the one as described for proficiency testing in the report 'iis Interlaboratory Studies: Protocol for the Organisation, Statistics and Evaluation' of June 2018 (iis-protocol, version 3.5).

For the statistical evaluation, the *unrounded* (when available) figures were used instead of the rounded test results. Test results reported as ‘<...’ or ‘>...’ were not used in the statistical evaluation.

First, the normality of the distribution of the various data sets per determination was checked by means of the Lilliefors-test, a variant of the Kolmogorov-Smirnov test and by the calculation of skewness and kurtosis. Evaluation of the three normality indicators in combination with the visual evaluation of the graphic Kernel density plot, lead to judgement of the normality being either ‘unknown’, ‘OK’, ‘suspect’ or ‘not OK’. After removal of outliers, this check was repeated. If a data set does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.

According to ISO 5726 the original test results per determination were submitted subsequently to Dixon's and/or Grubbs' and/or Rosner's outlier tests. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs' test and by R(0.01) for the Rosner's test. Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' test and by R(0.05) for the Rosner's test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.

For each assigned value, the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. In this PT, the criterion of ISO13528, paragraph 9.2.1 was met for all evaluated tests, therefore, the uncertainty of all assigned values may be neglibible and need not be included in the PT report.

Finally, the reproducibilities were calculated from the standard deviations by multiplying them with a factor of 2.8.

### 3.2 GRAPHICS

In order to visualize the data against the reproducibilities from literature, Gauss plots were made, using the sorted data for one determination (see appendix 1). On the Y-axis the reported test results are plotted. The corresponding laboratory numbers are on the X-axis. The straight horizontal line presents the consensus value (a trimmed mean). The four striped lines, parallel to the consensus value line, are the +3s, +2s, -2s and -3s target reproducibility limits of the selected reference test method. Outliers and other data, which were excluded from the calculations, are represented as a cross. Accepted data are represented as a triangle.

Furthermore, Kernel Density Graphs were made. The Kernel Density Graph is a method for producing a smooth density approximation to a set of data that avoids some problems associated with histograms. Also, a normal Gauss curve was projected over the Kernel Density Graph for reference.

### 3.3 Z-SCORES

To evaluate the performance of the participating laboratories the z-scores were calculated. As it was decided to evaluate the performance of the participants in this proficiency test (PT) against the literature requirements, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the variation in this interlaboratory study.

The target standard deviation was calculated from the literature reproducibility by division with 2.8. In case no literature reproducibility was available, other target values are used. In some cases, a reproducibility based on former iis proficiency tests could be used.

When a laboratory did use a test method with a reproducibility that is significantly different from the reproducibility of the reference test method used in this report, it is strongly advised

to recalculate the z-score, while using the reproducibility of the actual test method used, this in order to evaluate whether the reported test result is fit-for-use.

The z-scores were calculated according to:

$z_{(target)}$ = (test result - average of PT) / target standard deviation

The $z_{(target)}$ scores are listed in the result tables in appendix 1.

Absolute values for z<2 are very common and absolute values for z>3 are very rare. The usual interpretation of z-scores is as follows:

|z| < 1 good
1 < |z| < 2 satisfactory
2 < |z| < 3 questionable
3 < |z| unsatisfactory

## 4 EVALUATION

During the execution of this proficiency test no serious problems did occur. One participant did not report any test results. Not all laboratories were able to report all PAH requested. The eight laboratories reported in total 91 numerical test results. Observed were 6 outlying test results, which is 6.6%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.

Not all original data sets proved to have a normal Gaussian distribution. These are referred to as “not OK” or suspect”. The statistical evaluation of these data sets should be used with due care, see also paragraph 3.1.

### 4.1 EVALUATION PER SAMPLE AND PER COMPONENT

In this section the reported test results are discussed per sample and per component. The test methods, which were used by the various laboratories were taken into account for explaining the observed differences when possible and applicable. These test methods are also in the tables in appendix 1 together with the original data. The abbreviations used in these tables are listed in appendix 4.

Six participants reported to have used ZEK01.4-08 or AfPS GS 2014.
Regretfully, in the common test method ZEK01.4-08 and AfPS GS 2014:01 no precision data are mentioned. Neither in any other relevant standard test method for the determination of PAH. Therefore, it was decided to compare the calculated reproducibility against the reproducibility estimated from the Horwitz equation.

**Sample #18625:**

Total PAH: Only four participants reported a test result for this determination. Therefore, iis decided to calculate the total PAH for all reporting participants so that a statistical evaluation and z-scores could be performed. The obtained total PAH was in line with at least three of the four reported total PAH test results. When the calculated iis test results were evaluated, no statistical outliers were observed. The calculated reproducibility of the PAH calculated by iis is not in agreement with the target reproducibility using the Horwitz equation (based on 10 components).

Naphthalene: The determination may be problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the estimated target reproducibility using the Horwitz equation.

Acenaphthylene: The determination may be problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the estimated target reproducibility using the Horwitz equation.

Phenanthrene: The determination was not problematic. One statistical outlier was observed. However, the calculated reproducibility after rejection of the statistical outlier is in agreement with the estimated target reproducibility using the Horwitz equation.

Fluoranthene: The determination may be problematic. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the estimated target reproducibility using the Horwitz equation.

Pyrene: The determination may be problematic. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the estimated target reproducibility using the Horwitz equation.

Benzo[e]pyrene: The determination may be problematic. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the estimated target reproducibility using the Horwitz equation.

Benzo[a]pyrene: The determination may be problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the estimated target reproducibility using the Horwitz equation.

Benzo[g,h,i]perylene: Seven participants reported a test result. However, the calculated reproducibility is too large compared to the Horwitz equation.

Cyclopenta[c,d]pyrene: Three participants reported a test result. Regretfully, they differ much, therefore no z-scores were calculated.

For other PAH, the participants agreed on a concentration near or below the limit of detection. Therefore, no significant conclusions were drawn for these PAH (see appendix 2).

**Sample #18626:**

Total PAH: Only four participants reported a test result for this determination. Therefore, iis decided to calculate the total PAH for all reporting participants so that a statistical evaluation and z-scores could be performed. The obtained total PAH was in line with at least three of the four reported total PAH test results. When the calculated iis test results were evaluated, no statistical outliers were observed. The calculated reproducibility of the PAH calculated by iis is in full agreement with the target reproducibility using the Horwitz equation (based on 3 components).

Naphthalene: The determination may be problematic. No statistical outliers were observed. However, the calculated reproducibility is not in agreement with the estimated target reproducibility using the Horwitz equation.

Acenaphthylene: The determination may be problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is not in agreement with the estimated target reproducibility using the Horwitz equation.

Pyrene: The determination may be problematic. No statistical outliers were observed. However, the calculated reproducibility after rejection of the statistical outlier is not in agreement with the estimated target reproducibility using the Horwitz equation.

For other PAH, the participants agreed on a concentration near or below the limit of detection. Therefore, no significant conclusions were drawn for these PAH (see appendix 2).

### 4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the estimated target reproducibility using the Horwitz equation and the reproducibility as found for the group of participating laboratories. The number of significant test results, the average result, the calculated reproducibility (2.8*sd) and the estimated target reproducibility are presented in the next tables.

| Component | unit | n | average | 2.8 * sd | R(Horwitz) |
|---|---|---|---|---|---|
| Total PAH | mg/kg | 8 | 31.2 | 30.0 | 26.3 |
| Naphthalene | mg/kg | 7 | 2.2 | 1.8 | 0.9 |
| Acenaphthylene | mg/kg | 7 | 3.5 | 1.7 | 1.3 |
| Phenanthrene | mg/kg | 3 | 0.28 | 0.09 | 0.15 |
| Fluoranthene | mg/kg | 8 | 1.5 | 1.2 | 0.6 |
| Pyrene | mg/kg | 8 | 15.1 | 7.2 | 4.5 |
| Benzo[e]pyrene | mg/kg | 4 | 0.46 | 0.71 | 0.23 |
| Benzo[a]pyrene | mg/kg | 3 | 0.22 | 0.32 | 0.12 |

| Component | unit | n | average | 2.8 * sd | R(Horwitz) |
|---|---|---|---|---|---|
| Benzo[g,h,i]perylene | mg/kg | 7 | 2.8 | 4.8 | (1.1) |
| Cyclopenta[c,d]pyrene | mg/kg | 3 | (10.6) | (16.4) | n.a. |

Table 5: reproducibilities of components on sample #18625

| Component | unit | n | average | 2.8 * sd | R(Horwitz) |
|---|---|---|---|---|---|
| Total PAH | mg/kg | 8 | 13.6 | 7.1 | 7.1 |
| Naphthalene | mg/kg | 8 | 12.9 | 6.6 | 3.9 |
| Acenaphthylene | mg/kg | 5 | 0.25 | 0.48 | 0.14 |
| Pyrene | mg/kg | 7 | 0.39 | 0.23 | 0.20 |

Table 6: reproducibilities of components on sample #18626

Without further statistical calculations, it can be concluded that the group of participating laboratories may have problems with the analysis of PAH in tattoo ink at the evaluated concentration levels. See also the discussion in paragraphs 4.1 and 5.

### 4.3 UNCERTAINTIES OF THE PROFICIENCY TEST OF OCTOBER 2018

The uncertainty in the test results of the determination of PAH in tattoo ink in the iis18H01 PT are listed in the next table:

| Component | October 2018 | Target (Horwitz) 0.2 - 40 mg/kg |
|---|---|---|
| Total PAH | 12 – 34% | 19 – 32% |
| Naphthalene | 18 - 30% | 20 - 9% |
| Acenaphthylene | 17 - 70% | 20 - 9% |
| Acenaphthene | n.e. | 20 - 9% |
| Fluorene | n.e. | 20 - 9% |
| Phenanthrene | 12% | 20 - 9% |
| Anthracene | n.e. | 20 - 9% |
| Fluoranthene | 28% | 20 - 9% |
| Pyrene | 17 - 21% | 20 - 9% |
| Benzo[a]anthracene | n.e. | 20 - 9% |
| Chrysene | n.e. | 20 - 9% |
| Sum of Chrysene and Triphenylene | n.e. | 29 - 13% |
| Benzo[b]fluoranthene | n.e. | 20 - 9% |
| Benzo[j]fluoranthene | n.e. | 20 - 9% |
| Benzo[k]fluoranthene | n.e. | 20 - 9% |
| Sum of [b],[j] and [k] Benzofluoranthenes | n.e. | 35 - 16% |
| Benzo[e]pyrene | 55% | 20 - 9% |
| Benzo[a]pyrene | 53% | 20 - 9% |
| Indeno[1,2,3-c,d]pyrene | n.e. | 20 - 9% |
| Benzo[g,h,i]perylene | 62% | 20 - 9% |
| Dibenzo[a,h]anthracene | n.e. | 20 - 9% |
| Cyclopenta(c,d)pyrene | (55%) | 20 - 9% |

Table 7: development of relative uncertainties (RSD).

## 5 CONCLUSION

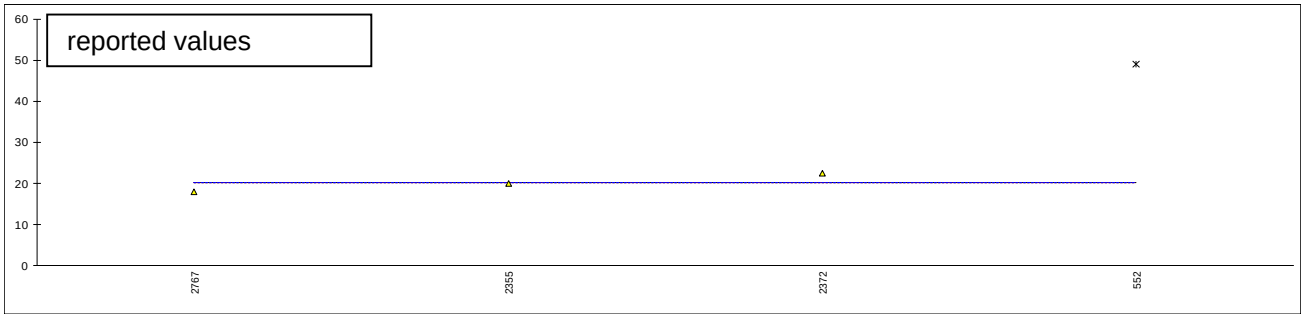
It is clear that all reporting laboratories would judge both samples the same and would reject both samples for too much PAH present in accordance with the resolution ResAP(2008)1 (limit of 0.5 mg/kg for most PAH).

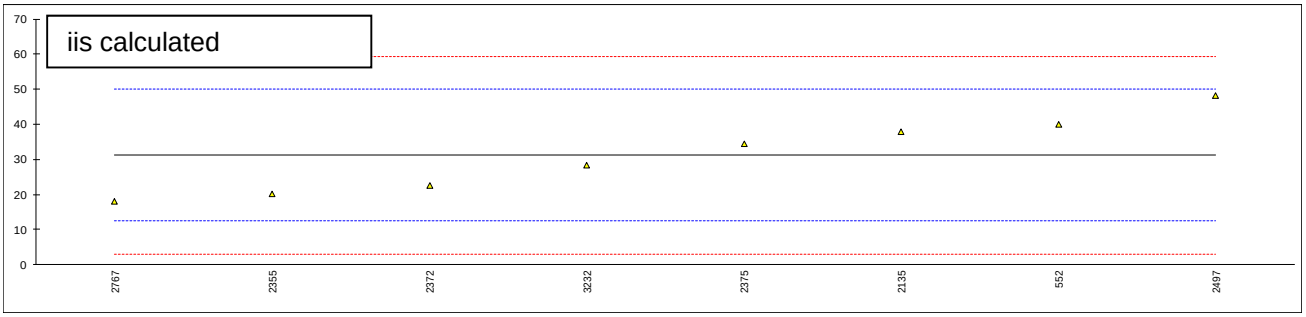
It can be concluded that the observed variation in this interlaboratory study may not be caused by just one critical point in the analysis. Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

## APPENDIX 1

Determination of Total PAH in sample #18625; results in mg/kg

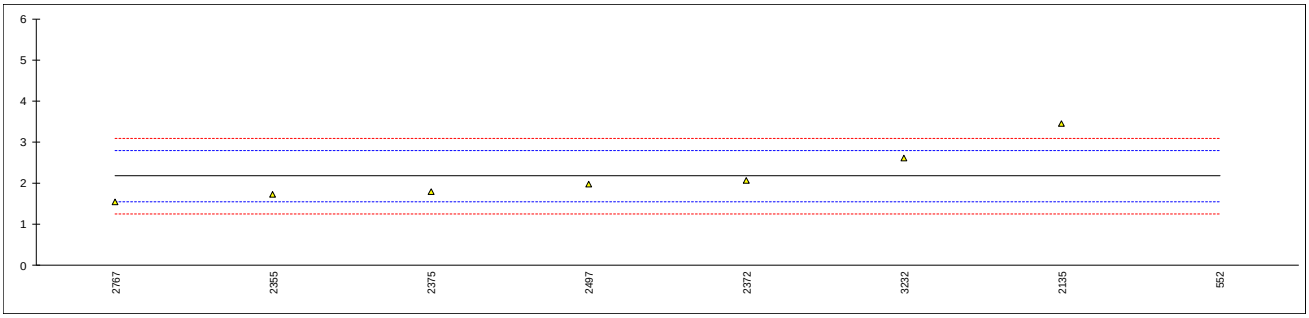
| lab | method | iis calc | mark | z(targ) | Orig. reported | remarks |
|---|---|---|---|---|---|---|
| 552 | AfPS GS 2014 | 39.905 | | 0.93 | 48.914 D(0.05),E | Calc error?iis calc 53.165 (not corrected results) |
| 2135 | In house | 37.998 | | 0.72 | ----- | |
| 2355 | AfPS GS 2014 | 20.1 | | -1.18 | 20.100 | |
| 2372 | AfPS GS 2014 | 22.574 | | -0.92 | 22.574 | |
| 2375 | AfPS GS 2014 | 34.36 | | 0.34 | ----- | |
| 2481 | | ----- | | ----- | ----- | |
| 2497 | EPA8270 | 48.292 | | 1.82 | ----- | |
| 2767 | ZEK01.4-08 | 17.93 | | -1.41 | 17.93 | |
| 3232 | AfPS GS 2014 | 28.34 | | -0.30 | ----- | |
| | normality | OK | | | unknown | |
| | n | 8 | | | 3 | |
| | outliers | 0 | | | 1 | |
| | mean (n) | 31.1874 | | | 20.2013 | |
| | st.dev. (n) | 10.73047 | RSD=34.4% | | 2.32366 | RSD=11.5% |
| | R(calc.) | 30.0453 | | | 6.5062 | |
| | st.dev.(Horwitz: n=10)) | 9.40229 | | | (6.50161) | |
| | R(Horwitz: n=10) | 26.3264. | | | (18.2045) | |

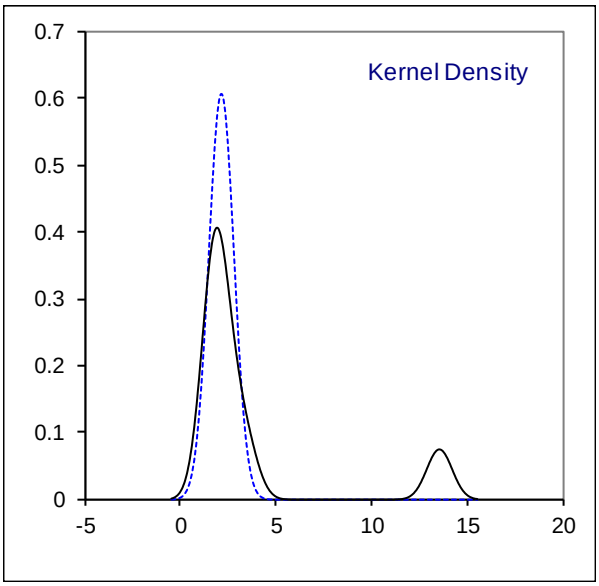


Determination of Naphthalene in sample #18625; results in mg/kg

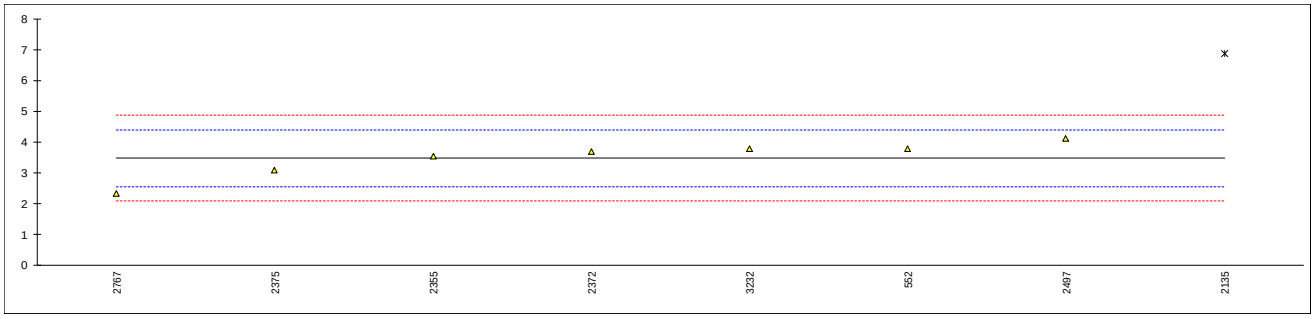
| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 552 | AfPS GS 2014 | 13.561 | G(0.01) | 36.85 | |
| 2135 | In house | 3.445 | | 4.12 | |
| 2355 | AfPS GS 2014 | 1.726 | | -1.44 | |
| 2372 | AfPS GS 2014 | 2.074 | | -0.31 | |
| 2375 | AfPS GS 2014 | 1.8 | C | -1.20 | First reported 1.982 |
| 2481 | | ----- | | ----- | |
| 2497 | EPA8270 | 1.982 | | -0.61 | |
| 2767 | ZEK01.4-08 | 1.55 | | -2.01 | |
| 3232 | AfPS GS 2014 | 2.62 | | 1.45 | |
| | | | | | |
| | normality | Not OK | | | |
| | n | 7 | | | |
| | outliers | 1 | | | |
| | mean (n) | 2.1709 | | | |
| | st.dev. (n) | 0.65727 | RSD=30.3% | | |
| | R(calc.) | 1.8403 | | | |
| | st.dev.(Horwitz) | 0.30909 | | | |
| | R(Horwitz) | 0.8654 | | | |

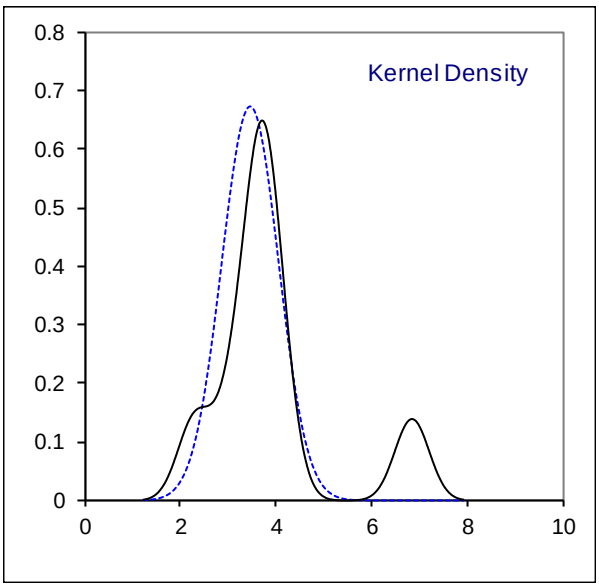


Determination of Acenaphthylene in sample #18625; results in mg/kg

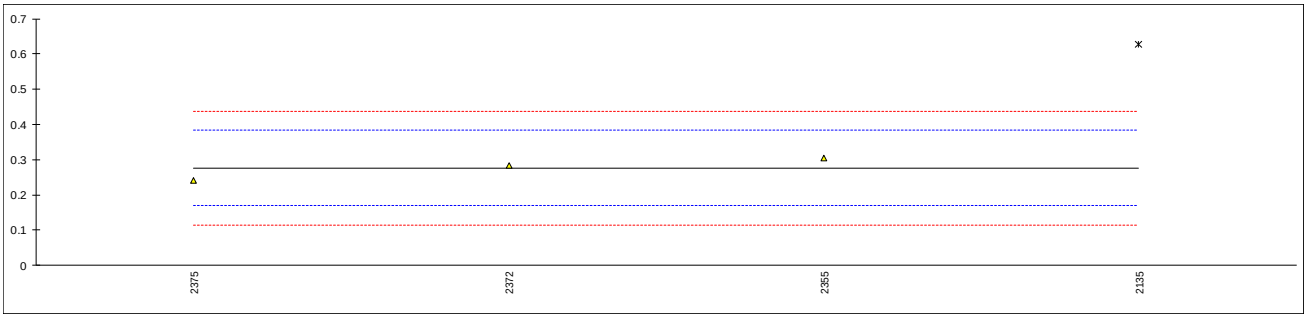
| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 552 | AfPS GS 2014 | 3.772 | | 0.65 | |
| 2135 | In house | 6.856 | G(0.05) | 7.34 | |
| 2355 | AfPS GS 2014 | 3.550 | | 0.16 | |
| 2372 | AfPS GS 2014 | 3.705 | | 0.50 | |
| 2375 | AfPS GS 2014 | 3.10 | | -0.81 | |
| 2481 | | ----- | | ----- | |
| 2497 | EPA8270 | 4.105 | | 1.37 | |
| 2767 | ZEK01.4-08 | 2.32 | | -2.51 | |
| 3232 | AfPS GS 2014 | 3.77 | | 0.64 | |
| | | | | | |
| | normality | Not OK | | | |
| | n | 7 | | | |
| | outliers | 1 | | | |
| | mean (n) | 3.4746 | | | |
| | st.dev. (n) | 0.59236 | RSD=17.0% | | |
| | R(calc.) | 1.6586 | | | |
| | st.dev.(Horwitz) | 0.46090 | | | |
| | R(Horwitz) | 1.2905 | | | |



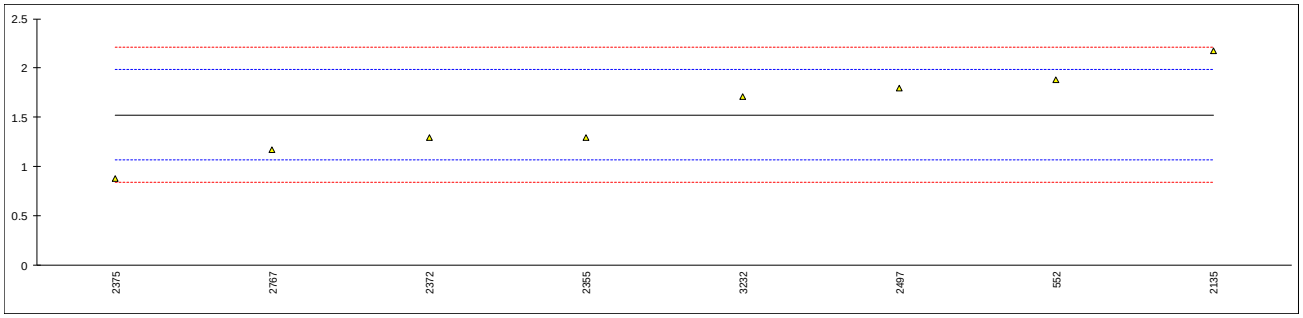
Determination of Phenanthrene in sample #18625; results in mg/kg

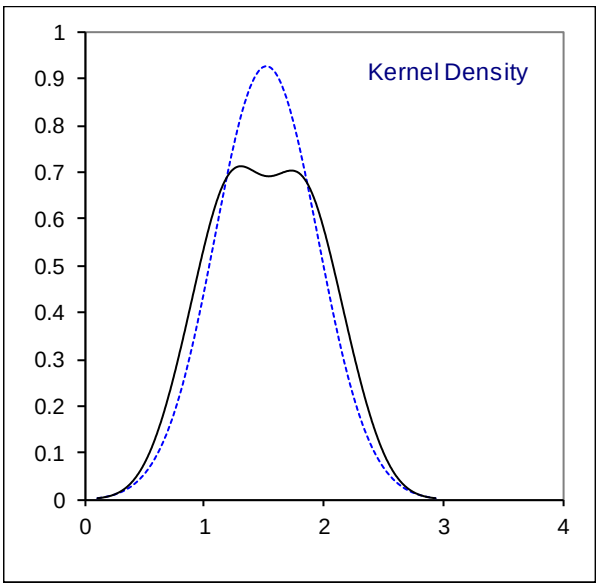
| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 552 | AfPS GS 2014 | ND | | ----- | |
| 2135 | In house | 0.626 | G(0.05) | 6.52 | |
| 2355 | AfPS GS 2014 | 0.305 | | 0.53 | |
| 2372 | AfPS GS 2014 | 0.284 | | 0.14 | |
| 2375 | AfPS GS 2014 | 0.24 | | -0.68 | |
| 2481 | | ----- | | ----- | |
| 2497 | | ----- | | ----- | |
| 2767 | | ----- | | ----- | |
| 3232 | AfPS GS 2014 | n.d | | ----- | |
| | | | | | |
| | normality | unknown | | | |
| | n | 3 | | | |
| | outliers | 1 | | | |
| | mean (n) | 0.2763 | | | |
| | st.dev. (n) | 0.03317 | RSD=12.0% | | |
| | R(calc.) | 0.0929 | | | |
| | st.dev.(Horwitz) | 0.05366 | | | |
| | R(Horwitz) | 0.1502 | | | |



Determination of Fluoranthene in sample #18625; results in mg/kg

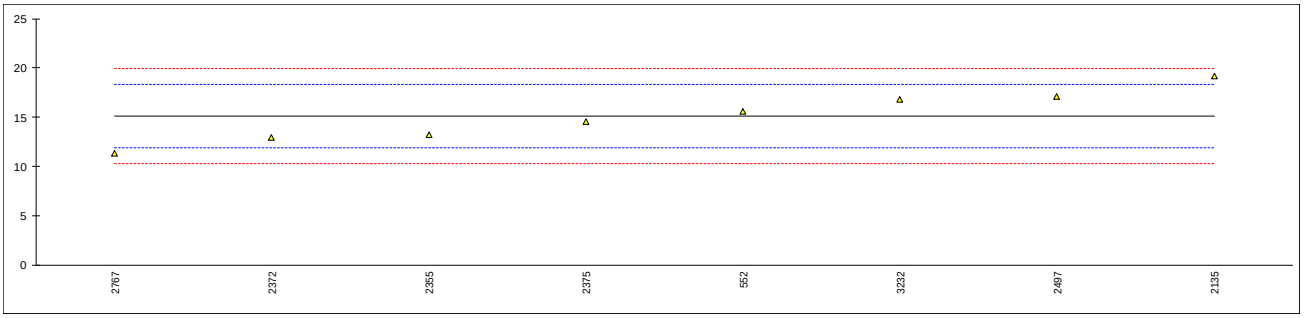
| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 552 | AfPS GS 2014 | 1.885 | | 1.57 | |
| 2135 | In house | 2.174 | | 2.83 | |
| 2355 | AfPS GS 2014 | 1.300 | | -0.99 | |
| 2372 | AfPS GS 2014 | 1.299 | | -0.99 | |
| 2375 | AfPS GS 2014 | 0.88 | | -2.82 | |
| 2481 | | ----- | | ----- | |
| 2497 | EPA8270 | 1.792 | | 1.16 | |
| 2767 | ZEK01.4-08 | 1.17 | | -1.55 | |
| 3232 | AfPS GS 2014 | 1.71 | | 0.80 | |
| | | | | | |
| | normality | OK | | | |
| | n | 8 | | | |
| | outliers | 0 | | | |
| | mean (n) | 1.5263 | | | |
| | st.dev. (n) | 0.43095 | RSD=28.2% | | |
| | R(calc.) | 1.2067 | | | |
| | st.dev.(Horwitz) | 0.22914 | | | |
| | R(Horwitz) | 0.6416 | | | |

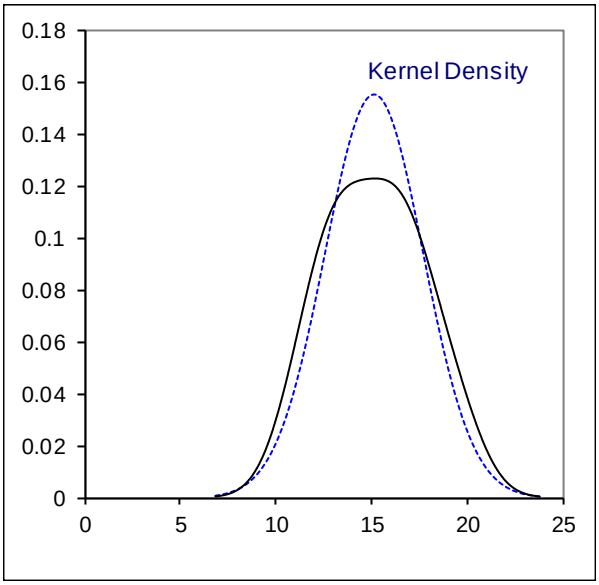


Determination of Pyrene in sample #18625; results in mg/kg

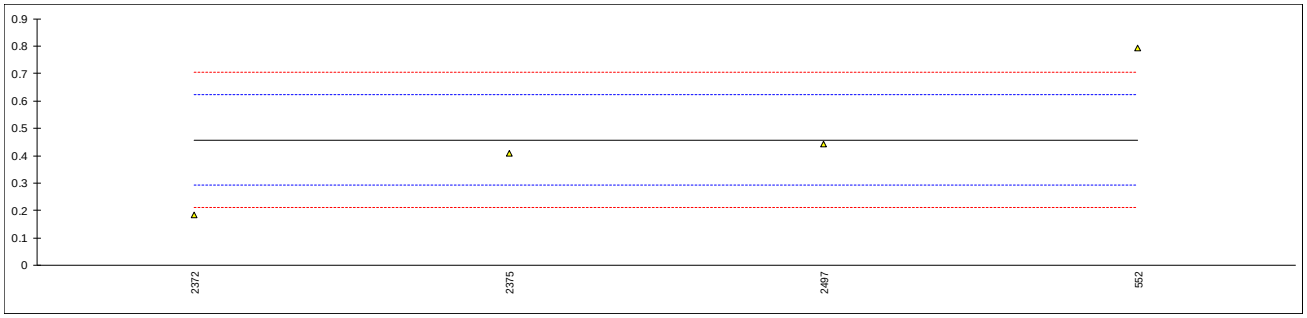
| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 552 | AfPS GS 2014 | 15.626 | C | 0.32 | First reported 28.885 |
| 2135 | In house | 19.188 | | 2.54 | |
| 2355 | AfPS GS 2014 | 13.220 | | -1.18 | |
| 2372 | AfPS GS 2014 | 12.947 | | -1.35 | |
| 2375 | AfPS GS 2014 | 14.59 | | -0.32 | |
| 2481 | | ----- | | ----- | |
| 2497 | EPA8270 | 17.114 | | 1.26 | |
| 2767 | ZEK01.4-08 | 11.39 | | -2.32 | |
| 3232 | AfPS GS 2014 | 16.82 | | 1.06 | |
| | | | | | |
| | normality | OK | | | |
| | n | 8 | | | |
| | outliers | 0 | | | |
| | mean (n) | 15.1117 | | | |
| | st.dev. (n) | 2.56890 | RSD=17.0% | | |
| | R(calc.) | 7.1929 | | | |
| | st.dev.(Horwitz) | 1.60668 | | | |
| | R(Horwitz) | 4.4987 | | | |



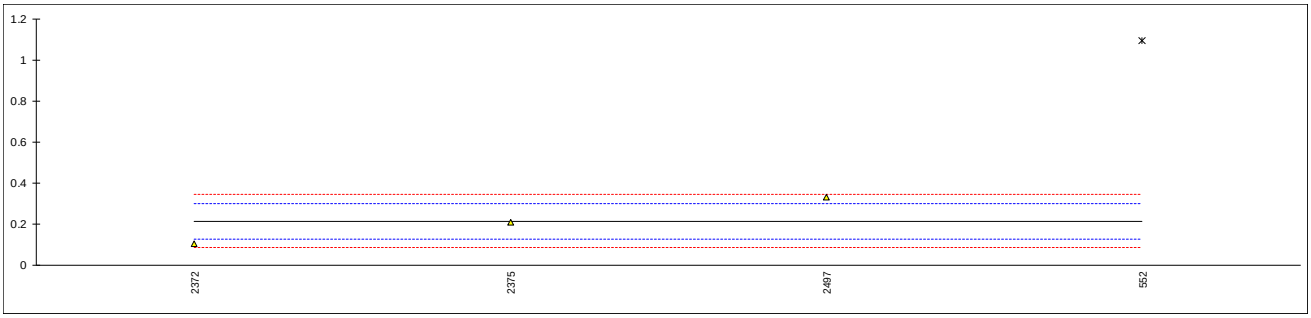
Determination of Benzo[e]pyrene in sample #18625; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 552 | AfPS GS 2014 | 0.794 | | 4.09 | |
| 2135 | | ----- | | ----- | |
| 2355 | AfPS GS 2014 | <0.1 | | <-4.34 | Possibly a false negative test result? |
| 2372 | AfPS GS 2014 | 0.183 | | -3.33 | |
| 2375 | AfPS GS 2014 | 0.41 | | -0.57 | |
| 2481 | | ----- | | ----- | |
| 2497 | EPA8270 | 0.442 | | -0.19 | |
| 2767 | | ----- | | ----- | |
| 3232 | | ----- | | ----- | |
| | normality | unknown | | | |
| | n | 4 | | | |
| | outliers | 0 | | | |
| | mean (n) | 0.4573 | | | |
| | st.dev. (n) | 0.26237 | RSD=55.2% | | |
| | R(calc.) | 0.7066 | | | |
| | st.dev.(Horwitz) | 0.08230 | | | |
| | R(Horwitz) | 0.2305 | | | |



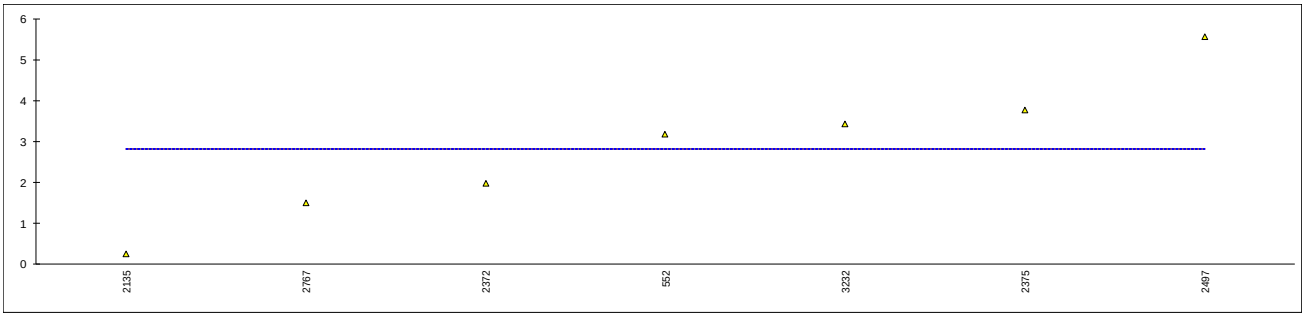
Determination of Benzo[a]pyrene in sample #18625; results in mg/kg

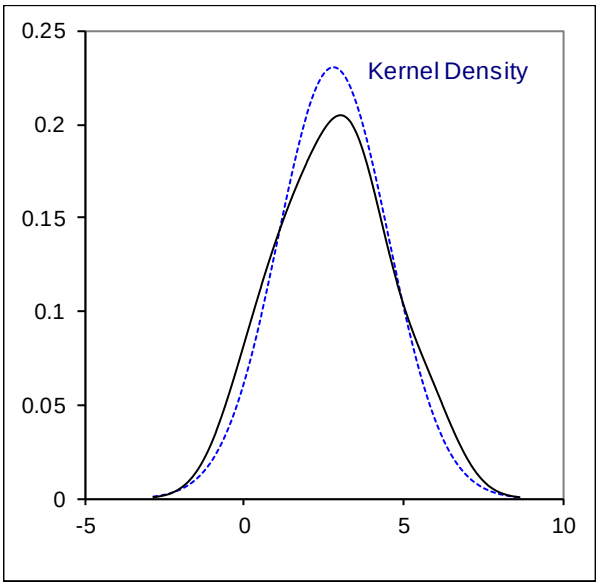
| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 552 | AfPS GS 2014 | 1.092 | G(0.01) | 20.23 | |
| 2135 | | ----- | | ----- | |
| 2355 | AfPS GS 2014 | <0.1 | | <-2.65 | |
| 2372 | AfPS GS 2014 | 0.103 | | -2.58 | |
| 2375 | AfPS GS 2014 | 0.21 | | -0.12 | |
| 2481 | | ----- | | ----- | |
| 2497 | EPA8270 | 0.332 | | 2.70 | |
| 2767 | | ----- | | ----- | |
| 3232 | AfPS GS 2014 | n.d | | ----- | |
| | | | | | |
| | normality | unknown | | | |
| | n | 3 | | | |
| | outliers | 1 | | | |
| | mean (n) | 0.2150 | | | |
| | st.dev. (n) | 0.11458 | RSD=53.3% | | |
| | R(calc.) | 0.3208 | | | |
| | st.dev.(Horwitz) | 0.04335 | | | |
| | R(Horwitz) | 0.1214 | | | |



Determination of Benzo[g,h,i]perylene in sample #18625; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 552 | AfPS GS 2014 | 3.176 | | ----- | |
| 2135 | In house | 0.243 | | ----- | |
| 2355 | | ----- | | ----- | |
| 2372 | AfPS GS 2014 | 1.979 | | ----- | |
| 2375 | AfPS GS 2014 | 3.76 | | ----- | |
| 2481 | | ----- | | ----- | |
| 2497 | EPA8270 | 5.562 | | ----- | |
| 2767 | ZEK01.4-08 | 1.5 | | ----- | |
| 3232 | AfPS GS 2014 | 3.42 | | ----- | |
| | | | | | |
| | normality | OK | | | |
| | n | 7 | | | |
| | outliers | 0 | | | |
| | mean (n) | 2.8057 | | | |
| | st.dev. (n) | 1.73100 | RSD=61.7% | | |
| | R(calc.) | 4.8468 | | | |
| | st.dev.(Horwitz) | (0.38435) | | | |
| | R(Horwitz) | (1.0762) | | | |



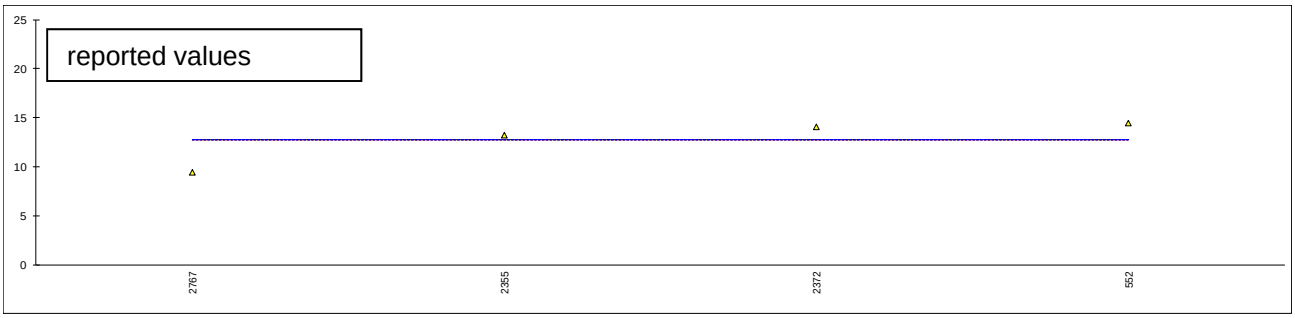



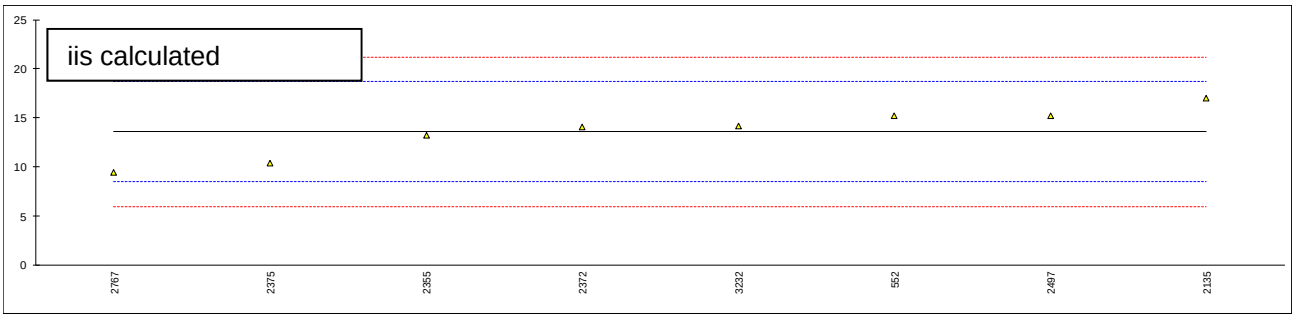
Determination of Cyclopenta[c,d]pyrene in sample #18625; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 552 | AfPS GS 2014 | ND | | ----- | |
| 2135 | In house | 5.466 | | ----- | |
| 2355 | | ----- | | ----- | |
| 2372 | AfPS GS 2014 | N/A | | ----- | |
| 2375 | AfPS GS 2014 | 9.37 | | ----- | |
| 2481 | | ----- | | ----- | |
| 2497 | EPA8270 | 16.963 | | ----- | |
| 2767 | | ----- | | ----- | |
| 3232 | | ----- | | ----- | |
| | | | | | |
| | normality | unknown | | | |
| | n | 3 | | | |
| | outliers | 0 | | | |
| | mean (n) | 10.5997 | | | |
| | st.dev. (n) | 5.84631 | RSD=55.2% | | |
| | R(calc.) | 16.3697 | | | |
| | st.dev.(lit) | n.a. | | | |
| | R(lit) | n.a. | | | |

## Determination of Total PAH in sample #18626; results in mg/kg

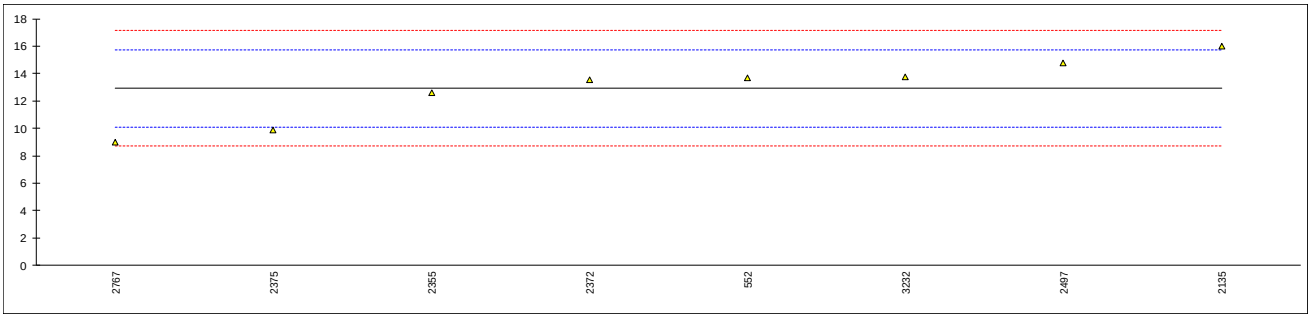
| lab | method | iis calc | mark | z(targ) | Orig. reported | remarks |
|---|---|---|---|---|---|---|
| 552 | AfPS GS 2014 | 15.198 | | 0.63 | 14.502 E | calc. error? iis calc 15.198 |
| 2135 | | 17.0135 | | 1.35 | ----- | |
| 2355 | AfPS GS 2014 | 13.195 | | -0.16 | 13.195 | |
| 2372 | AfPS GS 2014 | 14.098 | | 0.20 | 14.098 | |
| 2375 | | 10.37 | | -1.27 | ----- | |
| 2481 | | ----- | | ----- | ----- | |
| 2497 | | 15.269 | | 0.66 | ----- | |
| 2767 | ZEK01.4-08 | 9.46 | | -1.62 | 9.46 | |
| 3232 | | 14.14 | | 0.22 | ----- | |
| | normality | unknown | | | unknown | |
| | n | 8 | | | 4 | |
| | outliers | 0 | | | 0 | |
| | mean (n) | 13.5917 | | | 12.8137 | |
| | st.dev. (n) | 2.54203 | RSD=18.7% | | 2.30163 | RSD=18.0% |
| | R(calc.) | 7.1177 | | | 6.4446 | |
| | st.dev.(Horwitz: n=3) | 2.54319 | | | 2.41900 | |
| | R(Horwitz: n=3) | 7.1209 | | | 6.7732 | |

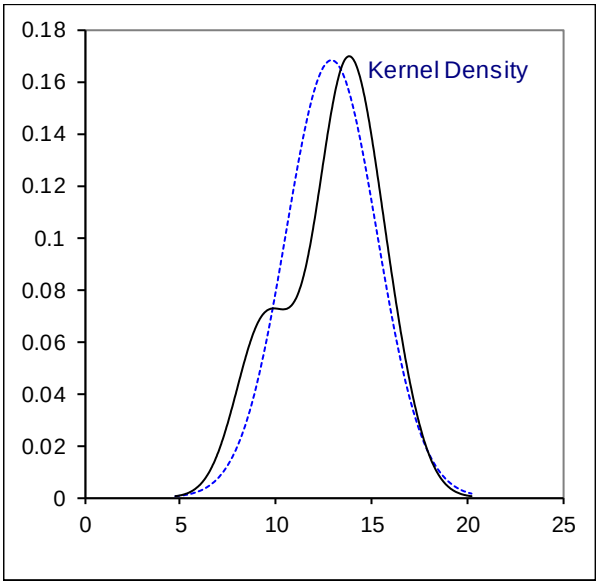


## Determination of Naphthalene in sample #18626; results in mg/kg

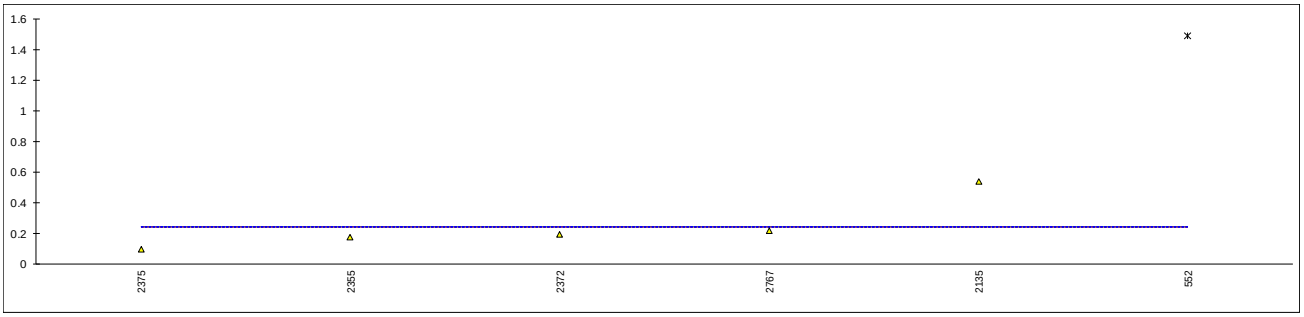
| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 552 | AfPS GS 2014 | 13.707 | | 0.57 | |
| 2135 | In house | 15.99 | | 2.19 | |
| 2355 | AfPS GS 2014 | 12.626 | | -0.20 | |
| 2372 | AfPS GS 2014 | 13.545 | | 0.45 | |
| 2375 | AfPS GS 2014 | 9.9 | C | -2.14 | First reported 18.97 |
| 2481 | | ----- | | ----- | |
| 2497 | EPA8270 | 14.778 | | 1.33 | |
| 2767 | ZEK01.4-08 | 9 | | -2.78 | |
| 3232 | AfPS GS 2014 | 13.75 | | 0.60 | |
| | | | | | |
| | normality | OK | | | |
| | n | 8 | | | |
| | outliers | 0 | | | |
| | mean (n) | 12.9119 | | | |
| | st.dev. (n) | 2.36490 | RSD=18.3% | | |
| | R(calc.) | 6.6218 | | | |
| | st.dev.(Horwitz) | 1.40569 | | | |
| | R(Horwitz) | 3.9359 | | | |



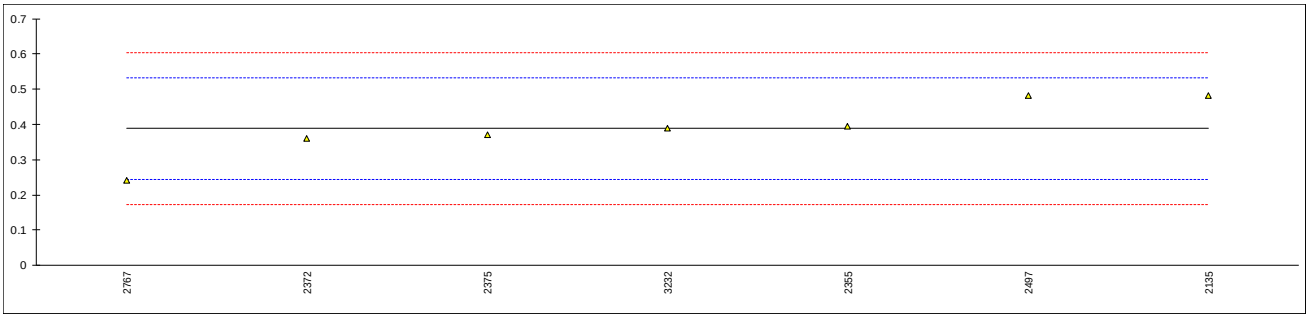
Determination of Acenapthylene in sample #18626; results in mg/kg

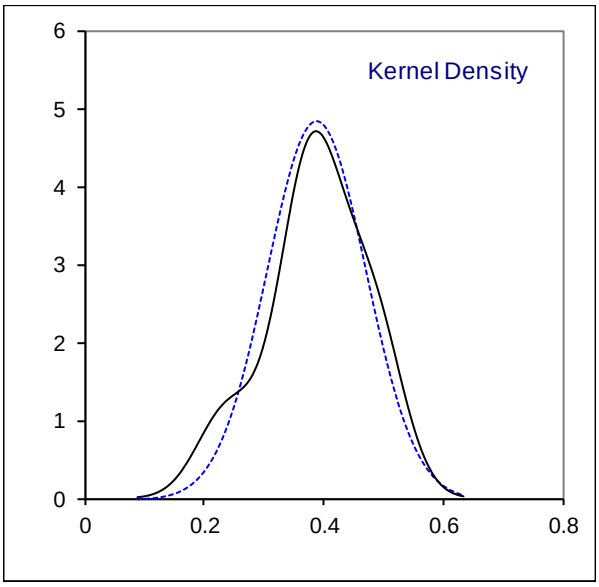
| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 552 | AfPS GS 2014 | 1.491 | G(0.05) | ----- | |
| 2135 | In house | 0.5405 | | ----- | |
| 2355 | AfPS GS 2014 | 0.175 | | ----- | |
| 2372 | AfPS GS 2014 | 0.193 | | ----- | |
| 2375 | AfPS GS 2014 | 0.10 | | ----- | |
| 2481 | | ----- | | ----- | |
| 2497 | | ----- | | ----- | |
| 2767 | ZEK01.4-08 | 0.22 | | ----- | |
| 3232 | AfPS GS 2014 | n.d | | ----- | |
| | | | | | |
| | normality | unknown | | | |
| | n | 5 | | | |
| | outliers | 1 | | | |
| | mean (n) | 0.2457 | | | |
| | st.dev. (n) | 0.17071 | RSD=69.5% | | |
| | R(calc.) | 0.4780 | | | |
| | st.dev.(Horwitz) | (0.04856) | | | |
| | R(Horwitz) | (0.1360) | | | |



Determination of Pyrene in sample #18626; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 552 | AfPS GS 2014 | ND | | ----- | |
| 2135 | In house | 0.483 | | 1.32 | |
| 2355 | AfPS GS 2014 | 0.395 | | 0.09 | |
| 2372 | AfPS GS 2014 | 0.36 | | -0.40 | |
| 2375 | AfPS GS 2014 | 0.37 | | -0.26 | |
| 2481 | | ----- | | ----- | |
| 2497 | EPA8270 | 0.481 | | 1.29 | |
| 2767 | ZEK01.4-08 | 0.24 | | -2.07 | |
| 3232 | AfPS GS 2014 | 0.39 | | 0.02 | |
| | | | | | |
| | normality | Suspect | | | |
| | n | 7 | | | |
| | outliers | 0 | | | |
| | mean (n) | 0.3884 | | | |
| | st.dev. (n) | 0.08240 | RSD=21.2% | | |
| | R(calc.) | 0.2307 | | | |
| | st.dev.(Horwitz) | 0.07165 | | | |
| | R(Horwitz) | 0.2006 | | | |



**APPENDIX 2**
Other reported PAHs

in sample #18625; results in mg/kg

| lab | Acenaphthene | Fluorene | Anthracene | Benzo(a) anthracene | Chrysene | Triphenylene | Chrysene + Triphenylene |
|---|---|---|---|---|---|---|---|
| 552 | ND | ND | ND | ND | ND | ND | ND |
| 2135 | ----- | ----- | 0.05 | ----- | ----- | ----- | ----- |
| 2355 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | ----- | ----- |
| 2372 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 2375 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 2481 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 2497 | ----- | ----- | 0.328 | ----- | ----- | ----- | ----- |
| 2767 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 3232 | n.d | n.d | n.d | n.d | n.d | ----- | ----- |

| lab | Benzo(b) fluoranthene | Benzo(j) fluoranthene | Benzo(k) fluoranthene | Sum benzo (b,j,k)fluoran | Indeno(1.2.3-c.d)pyrene | Dibenzo(a,h) anthracene |
|---|---|---|---|---|---|---|
| 552 | ND | ND | ND | ND | ND | ND |
| 2135 | ----- | ----- | ----- | ----- | ----- | ----- |
| 2355 | <0.1 | <0.1 | <0.1 | <0.3 | <0.1 | <0.1 |
| 2372 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 2375 | ----- | ----- | ----- | ----- | 0.26 | ----- |
| 2481 | ----- | ----- | ----- | ----- | ----- | ----- |
| 2497 | ----- | ----- | ----- | ----- | ----- | ----- |
| 2767 | ----- | ----- | ----- | ----- | ----- | ----- |
| 3232 | n.d | ----- | n.d | ----- | n.d | n.d |

in sample #18626; results in mg/kg

| lab | Acenaphthene | Fluorene | Phenanthrene | Anthracene | Fluoranthene | Benzo(a) anthracene | Chrysene |
|---|---|---|---|---|---|---|---|
| 552 | ND | ND | ND | ND | ND | ND | ND |
| 2135 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 2355 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| 2372 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 2375 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 2481 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 2497 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 2767 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 3232 | n.d | n.d | n.d | n.d | n.d | n.d | n.d |

| lab | Triphenylene | Chrysene + Triphenylene | Benzo(b) fluoranthene | Benzo(j) fluoranthene | Benzo(k) fluoranthene | Sum benzo (b,j,k)fluoran | Benzo(e) pyrene |
|---|---|---|---|---|---|---|---|
| 552 | ND | ND | ND | ND | ND | ND | ND |
| 2135 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 2355 | ----- | ----- | <0.1 | <0.1 | <0.1 | <0.3 | <0.1 |
| 2372 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| 2375 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 2481 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 2497 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 2767 | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 3232 | ----- | ----- | n.d | ----- | n.d | ----- | ----- |

| lab | Benzo(a) pyrene | Indeno(1.2.3-c.d)pyrene | Dibenzo(a,h) anthracene | Benzo(g,h,i) perylene | Cyclopenta (c,d)pyrene |
|---|---|---|---|---|---|
| 552 | ND | ND | ND | ND | ND |
| 2135 | ----- | ----- | ----- | ----- | ----- |
| 2355 | <0.1 | <0.1 | <0.1 | ----- | ----- |
| 2372 | n.d. | n.d. | n.d. | n.d. | N/A |
| 2375 | ----- | ----- | ----- | ----- | ----- |
| 2481 | ----- | ----- | ----- | ----- | ----- |
| 2497 | ----- | ----- | ----- | ----- | ----- |
| 2767 | ----- | ----- | ----- | ----- | ----- |
| 3232 | n.d | n.d | n.d | n.d | ----- |

## APPENDIX 3

### Number of participants per country

| | |
|---|---|
| 1 lab in | BRAZIL |
| 1 lab in | CHINA P.R. of |
| 1 lab in | FRANCE |
| 1 lab in | GERMANY |
| 1 lab in | INDIA |
| 1 lab in | ITALY |
| 1 lab in | TAIWAN R.O.C. |
| 2 labs in | TURKEY |

## APPENDIX 4

**Abbreviations**:

C = final test result after checking of first reported suspect test result
D(0.01) = outlier in Dixon's outlier test
D(0.05) = straggler in Dixon's outlier test
G(0.01) = outlier in Grubbs' outlier test
G(0.05) = straggler in Grubbs' outlier test
DG(0.01) = utlier in Double Grubbs' outlier test
DG(0.05) = straggler in Double Grubbs' outlier test
R(0.01) = outlier in Rosner's outlier test
R(0.05) = straggler in Rosner's outlier test
n.a. = not applicable
n.e. = not evaluated
n.d. = not detected
W = test result withdrawn on request of participant
ex = test result excluded from statistical evaluation
fr. = first reported

**Literature**:

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, June 2018
2 ASTM E178:02
3 ASTM E1301:03
4 ISO 5726:86
5 ISO 5726, parts 1-6, 1994
6 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
7 W.J. Youden and E.H. Steiner, Statistical Manual of the AOAC, (1975)
8 Horwitz. Journal of AOAC International Vol. 79 No.3. 1996
9 IP 367:96
10 DIN 38402 T41/42
11 ISO13528:2005 Statistical methods for use in proficiency testing by interlaboratory comparisons
12 W.J. Conover. Practical; Nonparametric Statistics. J. Wiley&Sons. NY. p.302. (1971)
13 P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)
14 J.N. Miller, Analyst, 118, 455, (1993)
15 Analytical Methods Committee Technical Brief, No 4 January 2001
16 P.J. Lowthian and M. Thompson, The Royal Society of Chemistry 2002, Analyst 2002, 127, 1359-1364.
17 R.G. Visser, Reliability of proficiency test results for metals and phthalates in plastics, Accred Qual Assur, 14:29-34 (2009)
18 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure,T*echnometrics*, 25(2), 165-172, (1983)