Institute for
Interlaboratory Studies

# Results of Proficiency Test
# Preservatives in Skin Care products
# (CMIT/MIT & Parabens)
# November 2022


**Organized by:** Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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# 1 INTRODUCTION

Preservatives may be used in cosmetics to prevent the growth of harmful bacteria and mold. Methylisothiazolinone (MIT) and Chloromethylisothiazolinone (CMIT), Parabens, Phenoxyethanol, Formaldehyde and Benzoic Acid are widely used as preservatives in liquid cosmetic and personal care products.
MIT and CMIT could be allergenic and cytotoxic, while Parabens and Phenoxyethanol are linked to hormonal disrupsion. Benzoic Acid is suspect for being the simplest aromatic carboxylic acid.
These preservatives in skin care products are regulated through Annex V of Regulation (EC) No 1223/2009 ("Cosmetics Regulation").

Since 2018 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the determination of MIT (2-Methyl-4-Isothiazolin-3-one) and CMIT (5-Chloro-2-Methyl-4-Isothiazolin-3-one) in Skin Care Products and for Parabens and other preservatives since 2019. During the annual testing program 2022/2023 it was decided to continue the proficiency test for the determination of Preservatives in Skin Care Products.

In this interlaboratory study 12 laboratories in 10 countries registered for participation, see appendix 3 for the number of participants per country. In this report the results of the Preservatives in Skin Care products proficiency test are presented and discussed. This report is also electronically available through the iis website www.iisnl.com.

# 2 SET UP

The Institute for Interlaboratory Studies (iis) in Spijkenisse, the Netherlands, was the organizer of this proficiency test (PT). Sample analyzes for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC17025 accredited laboratory.
It was decided to send one sample of Body Lotion in a 10 mL bottle labelled #22785 for the determination of CMIT and MIT and one sample of Body Milk in a 10 mL bottle labelled #22786 for the determination of individual Parabens and some other Preservatives.
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/IEC17043:2010. 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 regular basis by sending out questionnaires.

## 2.2 PROTOCOL

The protocol followed in the organization 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

A body lotion was purchased from a local supermarket and was artificially fortified with CMIT/MIT. After homogenization 25 PE bottles of 10 mL were filled with body lotion and labelled #22785.
The homogeneity of the subsamples was checked by determination of MIT using an in-house test method on four stratified randomly selected subsamples.

| | MIT<br>in mg/kg |
|---|---|
| sample #22785-1 | 9.46 |
| sample #22785-2 | 10.54 |
| sample #22785-3 | 9.79 |
| sample #22785-4 | 9.73 |

Table 1: homogeneity test results of subsamples #22785

From the above test results the relative standard deviation (RSD) was calculated and compared with 0.3 times the average relative standard deviation obtained from previous iis PTs of MIT in agreement with the procedure of ISO13528, Annex B2, in the next table.

| | MIT |
|---|---|
| RSD% (observed) | 4.7 |
| reference method | previous iis PTs |
| 0.3 x RSD% (ref. method) | 4.5 |

Table 2: evaluation of the relative standard deviation of subsamples #22785

The calculated relative standard deviation is in agreement with 0.3 times the average relative standard deviation obtained from the previous iis PTs. Therefore, homogeneity of the subsamples was assumed.

A body milk was purchased from a local supermarket and was artificially fortified with the preservatives: Ethylparaben, Propylparaben, Isobutylparaben and Phenoxyethanol. After homogenization 25 PE botlles of 10 mL were filled with body milk and labelled #22786.
The homogeneity of the subsamples was checked by determination of Propylparaben and Phenoxyethanol by using an in-house test method on five stratified randomly selected subsamples.

| | Propylparaben in mg/kg | Phenoxyethanol in mg/kg |
|---|---|---|
| sample #22786-1 | 189.6 | 9503 |
| sample #22786-2 | 191.8 | 9548 |
| sample #22786-3 | 190.9 | 9444 |
| sample #22786-4 | 192.3 | 9543 |
| sample #22786-5 | 192.6 | 9601 |

Table 3: homogeneity test results of subsamples #22786

From the above test results the relative standard deviations (RSD) were calculated and compared with 0.3 times the corresponding average relative standard deviation obtained from previous iis PTs of Preservatives in agreement with the procedure of ISO13528, Annex B2, in the next table.

| | Propylparaben | Phenoxyethanol |
|---|---|---|
| RSD% (observed) | 0.6 | 0.7 |
| reference method | previous iis PTs | previous iis PTs |
| 0.3 x RSD% (ref. method) | 2.7 | 2.7 |

Table 4: evaluation of the relative standard deviations of subsamples #22786

The calculated relative standard deviations are in agreement with 0.3 times the corresponding average relative standard deviation obtained from the previous iis PTs. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one body lotion sample labelled #22785 and one body milk sample labelled #22786 were sent on November 2, 2022.

## 2.5 ANALYZES

The participants were requested to determine on sample #22785 the concentrations of CMIT (5-Chloro-2-Methyl-4-Isothiazolin-3-one) and MIT (2-Methyl-4-Isothiazolin-3-one).
On sample #22786 was requested to determine the concentrations of Methylparaben as ester, Ethylparaben as ester, Propylparaben as ester, Isobutylparaben as ester, Butylparaben as ester, Phenoxyethanol, Formaldehyde and Benzoic acid.
It was also requested to report if the laboratory was accredited for this determination and to report the amount of sample intake.

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” test results, which are above the detection limit, because such test results cannot be used for meaningful statistical evaluation.

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 reference test methods (when applicable) 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 are also requested to confirm the 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 determination in appendix 1 of this report. The laboratories are presented by their 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 reanalyzes). Additional or corrected test results are used for data analysis and the original test 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 organization 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).
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 dataset does not have a normal distribution, the (results of the) statistical evaluation should be used with due care.

The assigned value is determined by consensus based on the test results of the group of participants after rejection of the statistical outliers and/or suspect data.

According to ISO13528 all (original received or corrected) results per determination were submitted to outlier tests. In the iis procedure for proficiency tests, outliers are detected prior to calculation of the mean, standard deviation and reproducibility. For small data sets, Dixon (up to 20 test results) or Grubbs (up to 40 test results) outlier tests can be used. For larger data sets (above 20 test results) Rosner's outlier test can be used. 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 negligible 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. This 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 (dotted line) was projected over the Kernel Density Graph (smooth line) for reference. The Gauss curve is calculated from the consensus value and the corresponding standard deviation.

### 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 (e.g. EN reproducibilities), 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 were used, like Horwitz or an estimated reproducibility based on former iis proficiency tests.

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 test result tables in appendix 1.

Absolute values for z<2 are very common and absolute values for z>3 are very rare. Therefore, 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

In this proficiency test no problems were encountered with the dispatch of the samples. All participants reported test results before the final reporting date. Not all participants were able to report all test results requested.
In total 12 participants reported 63 numerical test results. Observed were 3 outlying test results, which is 4.8% of the reported numerical test results. In proficiency tests outlier percentages of 3% - 7.5% are quite normal.

Not all 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 together with the original data in appendix 1. The abbreviations used in these tables are explained in appendix 4.

Unfortunately, a suitable reference test method providing the precision data is not available for all determinations. For these tests the calculated reproducibility was compared against the estimated reproducibility calculated with the Horwitz equation.

**sample #22785**

CMIT: The determination was not problematic. No statistical outliers were observed. The calculated reproducibility is in agreement with the estimated reproducibility calculated with the Horwitz equation.

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

**sample #22786**

One laboratory reported only three test results for this sample. One of which was an outlier and another was a possible false positive test result. Therefore, the third remaining test result was excluded from the statistical evaluation as all parabens are determined in one test run.

Methylparaben: This determination was not problematic. All reporting participants agreed on a value near or below the detection limit. Therefore, no z-scores are calculated.

Ethylparaben: This 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 reproducibility calculated with the Horwitz equation.

Propylparaben: This determination may be problematic. No statistical outliers were observed, but one test result was excluded. The calculated reproducibility after rejection of suspect data is not in agreement with the estimated reproducibility calculated with the Horwitz equation.

Isobutylparaben: This determination was not problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is in agreement with the estimated reproducibility calculated with the Horwitz equation.

Butylparaben: This determination was not problematic. All reporting participants except one agreed on a value near or below the detection limit. Therefore, no z-scores are calculated.

Phenoxyethanol: This determination may be problematic. No statistical outliers were observed. The calculated reproducibility is not in agreement with the estimated reproducibility calculated with the Horwitz equation.

Formaldehyde: Only a few participants reported a (non numerical) test result. Therefore, no z-scores are calculated.

Benzoic acid: This determination was not problematic. No statistical outliers were observed. The calculated reproducibility is in agreement with the estimated reproducibility calculated with the Horwitz equation.

### 4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as declared by the reference method and the reproducibility as found for the group of participating laboratories. The number of significant test results, the average, the calculated reproducibility (2.8 * standard deviation) and the target reproducibility derived from the reference method are presented in the next tables.

| Component | unit | n | average | 2.8 * sd | R(target) |
|---|---|---|---|---|---|
| CMIT | mg/kg | 10 | 31.7 | 5.9 | 8.4 |
| MIT | mg/kg | 9 | 11.7 | 3.9 | 3.6 |

Table 5: reproducibilities of tests on sample #22785

| Component | unit | n | average | 2.8 * sd | R(target) |
|---|---|---|---|---|---|
| Methylparaben | mg/kg | 7 | <5 | n.e. | n.e. |
| Ethylparaben | mg/kg | 10 | 211 | 52 | 42 |
| Propylparaben | mg/kg | 9 | 210 | 86 | 42 |
| Isobutylparaben | mg/kg | 6 | 306 | 48 | 58 |
| Butylparaben | mg/kg | 6 | <5 | n.e. | n.e. |
| Phenoxyethanol | mg/kg | 8 | 10399 | 2143 | 1158 |
| Formaldehyde | mg/kg | 2 | not detected | n.e. | n.e. |
| Benzoic acid | mg/kg | 7 | 900 | 71 | 145 |

Table 6: reproducibilities of tests on sample #22786

Without further statistical calculations it can be concluded that for a number of components there is a good compliance of the group of participating laboratories with the target reproducibility. The problematic tests have been discussed in paragraph 4.1.

### 4.3 COMPARISON OF THE PROFICIENCY TEST OF NOVEMBER 2022 WITH PREVIOUS PTS

| | November 2022 | November 2021 | November 2020 | November 2019**) | November 2018*) |
|---|---|---|---|---|---|
| Number of reporting laboratories | 12 | 16 | 16 | 13 / 13 | 6 |
| Number of test results | 63 | 95 | 82 | 26 / 67 | 12 |
| Number of statistical outliers | 3 | 7 | 8 | 0 / 3 | 2 |
| Percentage of statistical outliers | 4.8% | 7.4% | 9.8% | 0% / 4.5% | 17% |

Table 7: comparison with previous proficiency tests

*) CMIT/MIT only

*) PT for CMIT/MIT / PT for Preservatives in Skin Care separately

In proficiency tests outlier percentages of 3% - 7.5% are quite normal.

The performance of the determinations of the proficiency test was compared to uncertainties observed in PTs over the years, expressed as relative standard deviation (RSD) of the PTS, see next table.

| Component | November 2023 | November 2021 | November 2020 | 2019 -2018 | Target Horwitz |
|---|---|---|---|---|---|
| CMIT | 7% | 11% | 8% | 10-20% | 10% |
| MIT | 12% | 12% | 10% | 19% | 12% |
| Methylparaben | --- | 6% | 6% | 13% | 6% |
| Ethylparaben | 9% | --- | 7% | 11% | 7-10% |
| Propylparaben | 15% | 6% | 5% | 12% | 8% |
| Isobutylparaben | 7% | 7% | 14% | 14% | 8% |
| Butylparaben | --- | 14% | 3% | 7% | 8% |
| Phenoxyethanol | 7% | 4% | 8% | 12% | 4% |
| Benzoic acid | 6% | 7% | --- | --- | 6% |

Table 8: development of the uncertainties over the years

It is observed that the variation is in general in line with previous iis PTs, except for Propylparaben and Phenoxyethanol.

### 4.4 EVALUATION OF THE ANALYTICAL DETAILS

For this PT some analytical details were requested. The reported answers are listed in appendix 2. Based on these answers the following can be summarized:

For the determination of CMIT/MIT eight participants mentioned that they are accredited for this determination. Six participants used 1 gram or less for sample intake and three others used an intake of 2 grams or more.

For the determination of Parabens six participants mentioned that they are accredited for this determination. Nine participants used 1 gram or less for sample intake and two others used an intake of 2 grams or more.

## 5 DISCUSSION

The participants were able to detect CMIT/MIT and several Preservatives in this proficiency test. Limits for the presence Preservatives in Skin Care Products have been set through Annex V of Regulation (EC) No 1223/2009 ("Cosmetics Regulation") from 30-11-2009 and last updated on 17-12-2022.

| Component | Rinse-off product | Leave-on product |
|---|---|---|
| CMIT:MIT 3:1 | 15 mg/kg (0.0015%) | shall not contain |
| MIT | 15 mg/kg (0.0015%) | shall not contain |

Table 9: limits for CMIT/MIT in Commission Regulation (EU) 1223/2009, Annex V, entry 39 and 57 respectively

Note from Annex V: the use of the mixture is incompatible with the use of MIT alone in the same product

Sample #22785 is a body lotion and thus a leave-on product. Since the use of CMIT/MIT in Annex V is only specified for rinse-off products, it is stated in article 14d of the same regulation that if used for anything other than rinse-off, it should not contain CMIT/MIT.
All reporting participants would have rejected sample #22785 because of the detected presence of CMIT/MIT in the sample.

| Components | Limit in mg/kg |
|---|---|
| Isobutylparaben (Annex II, entry 1375) | prohibited |
| Methylparaben and Ethylparaben (Annex V, entry 12)<br>- for single ester<br>- for mixtures of esters | <br>4000<br>8000 |
| Propylparaben and Butylparaben (Annex V, entry 12a)<br>- sum of individual concentrations<br>- mixtures entry 12 and 12a | <br>1400<br>8000 |
| Phenoxyethanol (Annex V, entry 29) | 10000 |
| Formaldehyde (Annex II, entry 1577) | prohibited |
| Benzoic acid (Annex V, entry 1)<br>- leave-on products<br>- rinse-off products | <br>5000<br>25000 |

Table 10: limits for Preservatives in Commission Regulation (EU) 1223/2009

It is observed that eight of the eleven reporting participants would judge sample #22786 in the same way and reject the sample for the presence of Isobutylparaben and level of Phenoxyethanol above the limit in accordance with the Annex V of Regulation (EC) No 1223/2009. Remarkably, three other participants only reported test results for Ethylparaben, Propylparaben and Butylparaben and may have accepted this sample based on only these determinations.

## 6 CONCLUSION

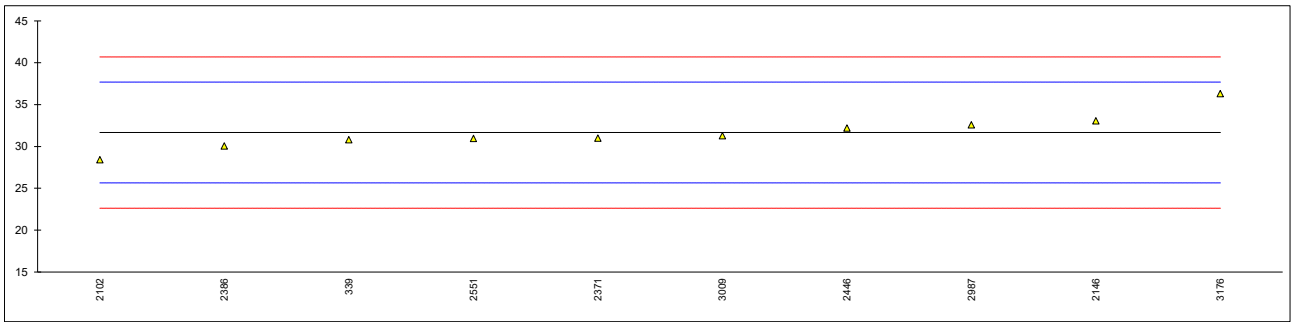
No reference materials for CMIT or MIT and for individual Parabens in cosmetics are available to optimise the determination of CMIT/MIT or Parabens. As an alternative, participation in a proficiency test may enable the laboratories to check their performance and thus to increase this comparability.

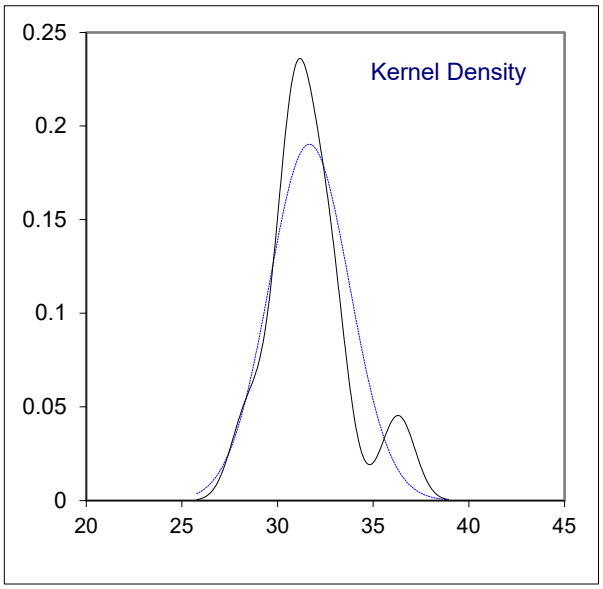
The observed variation in this interlaboratory study may not be caused by just one critical point in the analysis. Each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary. Therefore, participation on a regular basis in this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

**APPENDIX 1**

Determination of CMIT (5-Chloro-2-Methyl-4-Isothiazolin-3-one) CAS No. 26172-55-4 in sample #22785; results in mg/kg

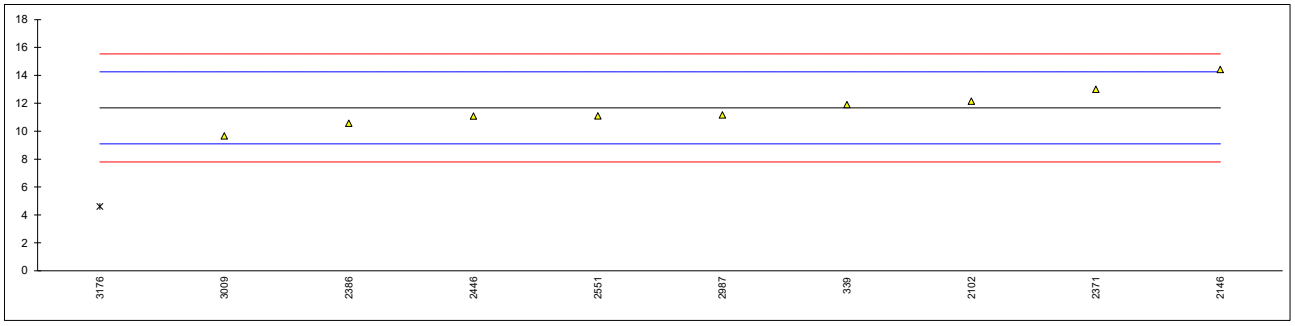
| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 339 | In house | 30.8 | | -0.29 | |
| 2102 | In house | 28.41 | | -1.08 | |
| 2146 | In house | 33.053 | | 0.46 | |
| 2278 | | ----- | | ----- | |
| 2371 | TFDA | 31.0 | | -0.22 | |
| 2386 | In house | 30.04 | | -0.54 | |
| 2446 | | 32.185 | | 0.17 | |
| 2551 | In house | 30.951 | | -0.24 | |
| 2987 | In house | 32.5605 | | 0.30 | |
| 3009 | In house | 31.29 | | -0.12 | |
| 3166 | | ----- | | ----- | |
| 3176 | In house | 36.30 | C | 1.54 | first reported: 25.2 |
| | | | | | |
| | normality | not OK | | | |
| | n | 10 | | | |
| | outliers | 0 | | | |
| | mean (n) | 31.6589 | | | |
| | st.dev. (n) | 2.09651 | RSD = 6.6% | | |
| | R(calc.) | 5.8702 | | | |
| | st.dev.(Horwitz) | 3.01141 | | | |
| | R(Horwitz) | 8.4319 | | | |

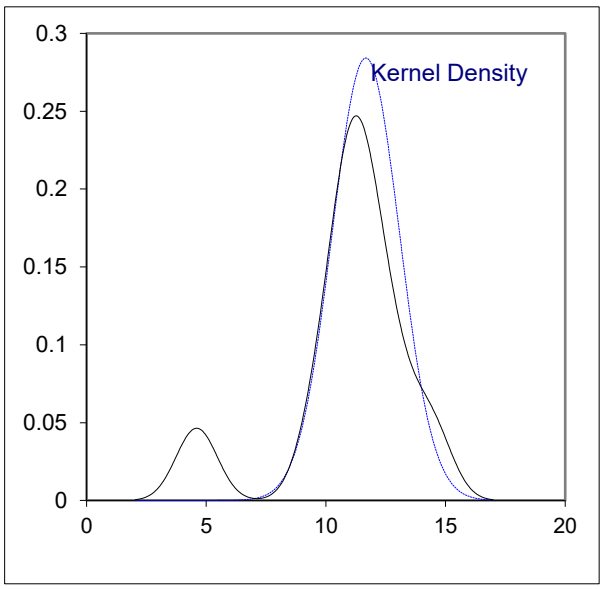


Determination of MIT (2-Methyl-4-Isothiazolin-3-one) CAS No. 2682-20-4 in sample #22785; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 339 | In house | 11.9 | | 0.18 | |
| 2102 | In house | 12.15 | | 0.37 | |
| 2146 | In house | 14.412 | | 2.13 | |
| 2278 | | ----- | | ----- | |
| 2371 | TFDA | 13.0 | | 1.03 | |
| 2386 | In house | 10.56 | | -0.86 | |
| 2446 | | 11.090 | | -0.45 | |
| 2551 | In house | 11.096 | | -0.44 | |
| 2987 | In house | 11.1568 | | -0.40 | |
| 3009 | In house | 9.66 | | -1.56 | |
| 3166 | | ----- | | ----- | |
| 3176 | In house | 4.6 | C,D(0.05) | -5.48 | first reported: 2.04 |
| | normality | OK | | | |
| | n | 9 | | | |
| | outliers | 1 | | | |
| | mean (n) | 11.6694 | | | |
| | st.dev. (n) | 1.40411 | RSD = 12.0% | | |
| | R(calc.) | 3.9315 | | | |
| | st.dev.(Horwitz) | 1.28992 | | | |
| | R(Horwitz) | 3.6118 | | | |



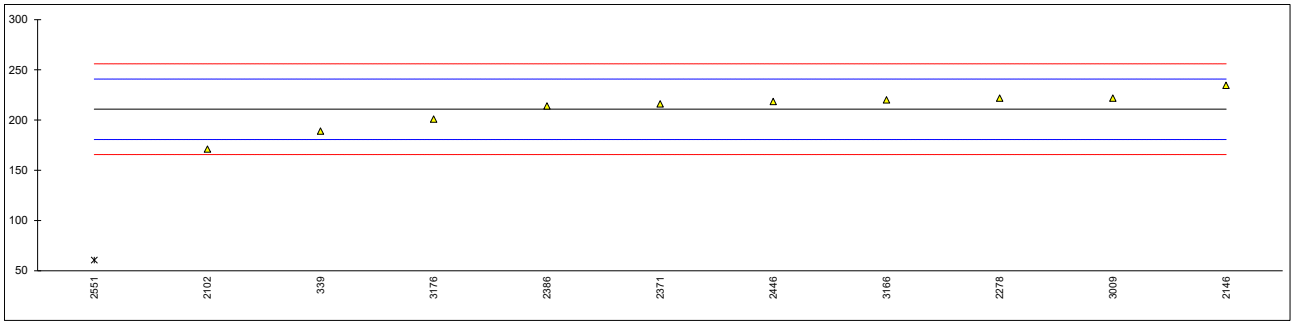



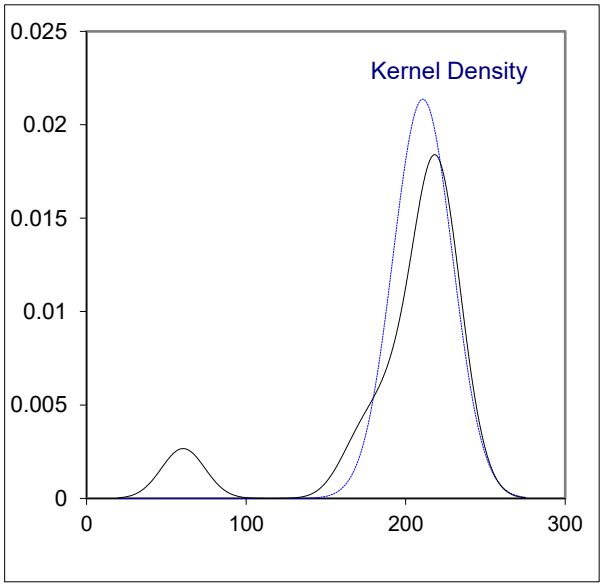
Determination of Methylparaben as ester CAS No. 99-76-3 in sample #22786; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 339 | In house | not detected | | ----- | |
| 2102 | In house | Not detected | | ----- | |
| 2146 | In house | <2 | | ----- | |
| 2278 | | ----- | | ----- | |
| 2371 | TFDA | not determined | | ----- | |
| 2386 | In house | <5 | | ----- | |
| 2446 | In house | not detected | | ----- | |
| 2551 | | ----- | | ----- | |
| 2987 | | ----- | | ----- | |
| 3009 | In house | not detected | | ----- | |
| 3166 | In house | ND | | ----- | |
| 3176 | | ----- | | ----- | |

Determination of Ethylparaben as ester CAS No. 120-47-8 in sample #22786; results in mg/kg

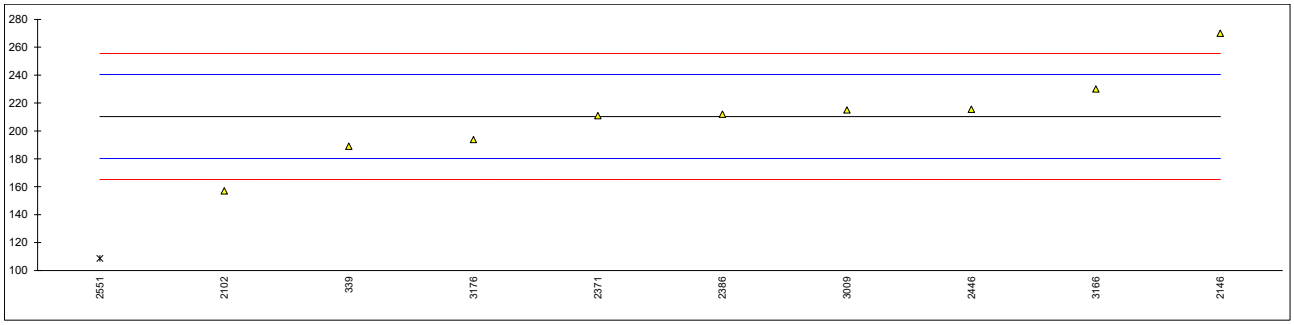
| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 339 | In house | 189 | | -1.44 | |
| 2102 | In house | 171 | | -2.64 | |
| 2146 | In house | 234.491 | | 1.58 | |
| 2278 | In house | 221.730 | | 0.73 | |
| 2371 | TFDA | 216 | | 0.35 | |
| 2386 | In house | 214 | | 0.22 | |
| 2446 | In house | 218.489 | | 0.51 | |
| 2551 | In house | 60.511 | G(0.01) | -9.97 | |
| 2987 | | ----- | | ----- | |
| 3009 | In house | 221.8 | | 0.73 | |
| 3166 | In house | 220 | | 0.61 | |
| 3176 | In house | 200.95 | | -0.65 | |
| | | | | | |
| | normality | suspect | | | |
| | n | 10 | | | |
| | outliers | 1 | | | |
| | mean (n) | 210.7460 | | | |
| | st.dev. (n) | 18.67572 | RSD = 8.9% | | |
| | R(calc.) | 52.2920 | | | |
| | st.dev.(Horwitz) | 15.07019 | | | |
| | R(Horwitz) | 42.1965 | | | |

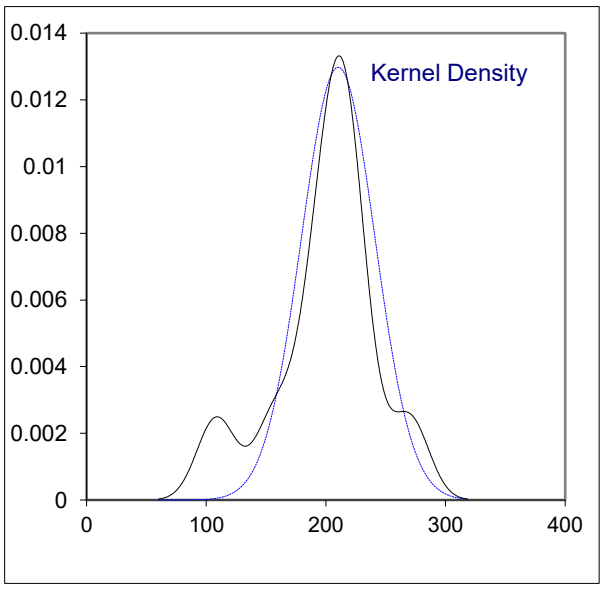


Determination of Propylparaben as ester CAS No. 94-13-3 in sample #22786; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 339 | In house | 189 | | -1.42 | |
| 2102 | In house | 157 | | -3.55 | |
| 2146 | In house | 269.967 | | 3.96 | |
| 2278 | | ----- | | ----- | |
| 2371 | TFDA | 211 | | 0.04 | |
| 2386 | In house | 211.9 | | 0.10 | |
| 2446 | In house | 215.572 | | 0.35 | |
| 2551 | In house | 108.541 | ex | -6.77 | test result excluded, see §4.1 |
| 2987 | | ----- | | ----- | |
| 3009 | In house | 215.0 | | 0.31 | |
| 3166 | In house | 230 | | 1.31 | |
| 3176 | In house | 193.82 | | -1.10 | |
| | | | | | |
| | normality | suspect | | | |
| | n | 9 | | | |
| | outliers | 0 (+1ex) | | | |
| | mean (n) | 210.3621 | | | |
| | st.dev. (n) | 30.75571 | RSD = 14.6% | | |
| | R(calc.) | 86.1160 | | | |
| | st.dev.(Horwitz) | 15.04687 | | | |
| | R(Horwitz) | 42.1312 | | | |

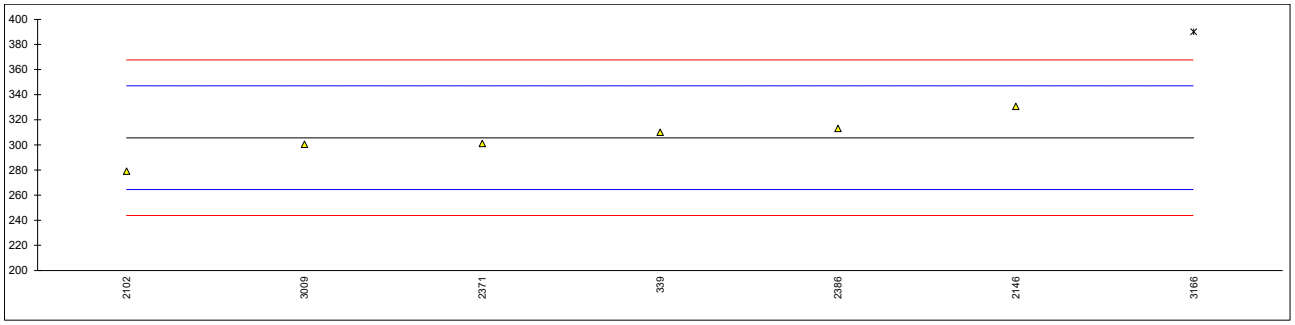


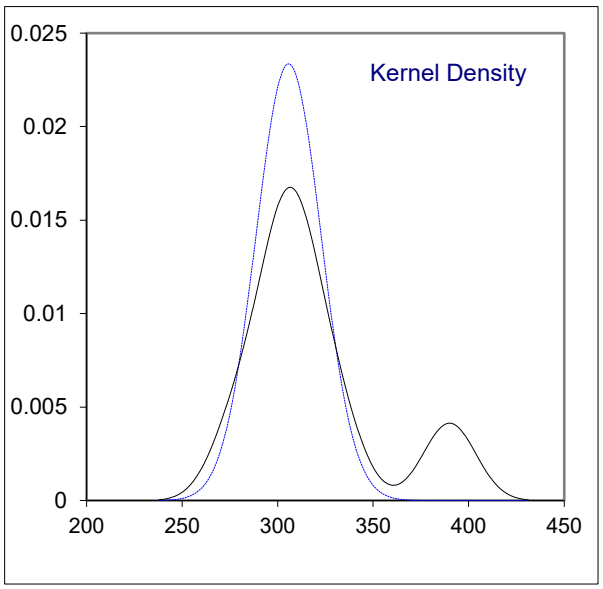



Determination of Isobutylparaben as ester CAS No. 4247-02-3 in sample #22786; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 339 | In house | 310 | | 0.21 | |
| 2102 | In house | 279 | | -1.29 | |
| 2146 | In house | 330.710 | | 1.21 | |
| 2278 | | ----- | | ----- | |
| 2371 | TFDA | 301 | | -0.23 | |
| 2386 | In house | 313 | | 0.35 | |
| 2446 | | ----- | | ----- | |
| 2551 | | ----- | | ----- | |
| 2987 | | ----- | | ----- | |
| 3009 | In house | 300.5 | | -0.25 | |
| 3166 | In house | 390 | G(0.05) | 4.08 | |
| 3176 | | ----- | | ----- | |

| | |
|---|---|
| normality | unknown |
| n | 6 |
| outliers | 1 |
| mean (n) | 305.7017 |
| st.dev. (n) | 17.08391 RSD = 5.6% |
| R(calc.) | 47.8349 |
| st.dev.(Horwitz) | 20.67013 |
| R(Horwitz) | 57.8764 |



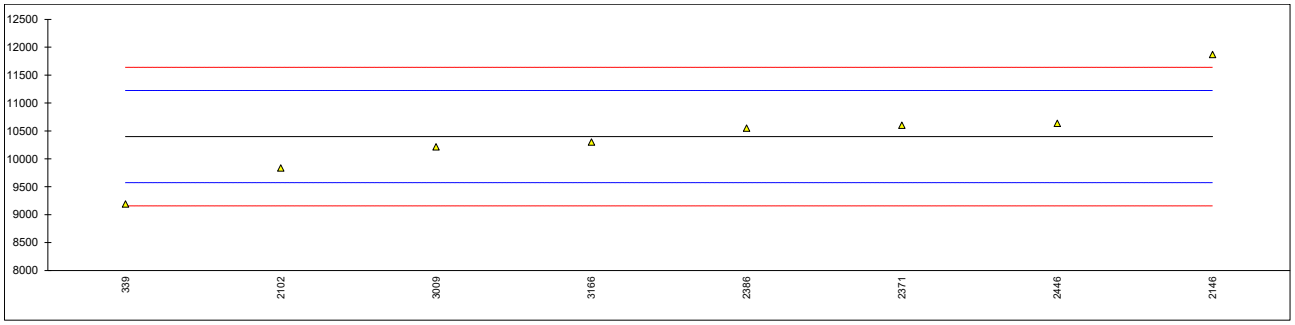



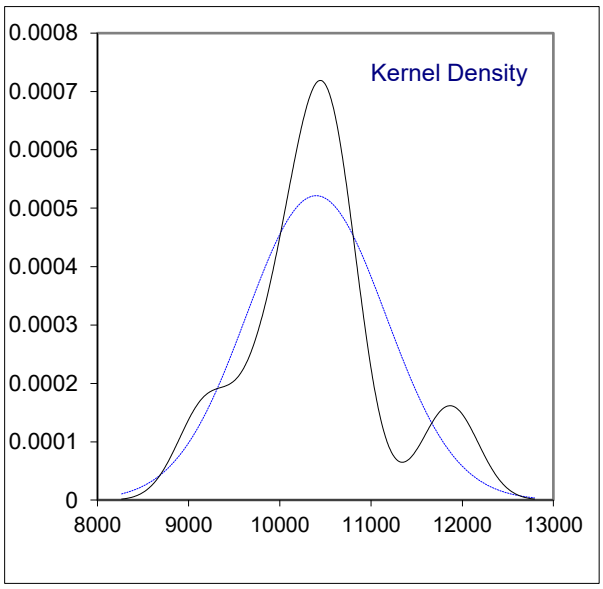
Determination of Butylparaben as ester CAS No. 94-26-8 in sample #22786; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 339 | In house | not detected | | ----- | |
| 2102 | In house | Not detected | | ----- | |
| 2146 | In house | <2 | | ----- | |
| 2278 | | ----- | | ----- | |
| 2371 | TFDA | not determined | | ----- | |
| 2386 | In house | <5 | | ----- | |
| 2446 | | ----- | | ----- | |
| 2551 | In house | 77.952 | f+? | ----- | possible false positive test result? |
| 2987 | | ----- | | ----- | |
| 3009 | In house | not detected | | ----- | |
| 3166 | In house | Not detected | | ----- | |
| 3176 | | ----- | | ----- | |

Determination of Phenoxyethanol CAS No. 122-99-6 in sample #22786; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 339 | In house | 9190 | | -2.92 | |
| 2102 | In house | 9836 | | -1.36 | |
| 2146 | In house | 11868.064 | C | 3.55 | first reported: 12686.991 |
| 2278 | | ----- | | ----- | |
| 2371 | TFDA | 10600 | | 0.49 | |
| 2386 | In house | 10548 | | 0.36 | |
| 2446 | In house | 10634.851 | | 0.57 | |
| 2551 | | ----- | | ----- | |
| 2987 | | ----- | | ----- | |
| 3009 | In house | 10213.3 | | -0.45 | |
| 3166 | In house | 10300 | | -0.24 | |
| 3176 | | ----- | | ----- | |
| | normality | unknown | | | |
| | n | 8 | | | |
| | outliers | 0 | | | |
| | mean (n) | 10398.776 | | | |
| | st.dev. (n) | 765.2556 | RSD = 7.4% | | |
| | R(calc.) | 2142.716 | | | |
| | st.dev.(Horwitz) | 413.5101 | | | |
| | R(Horwitz) | 1157.828 | | | |



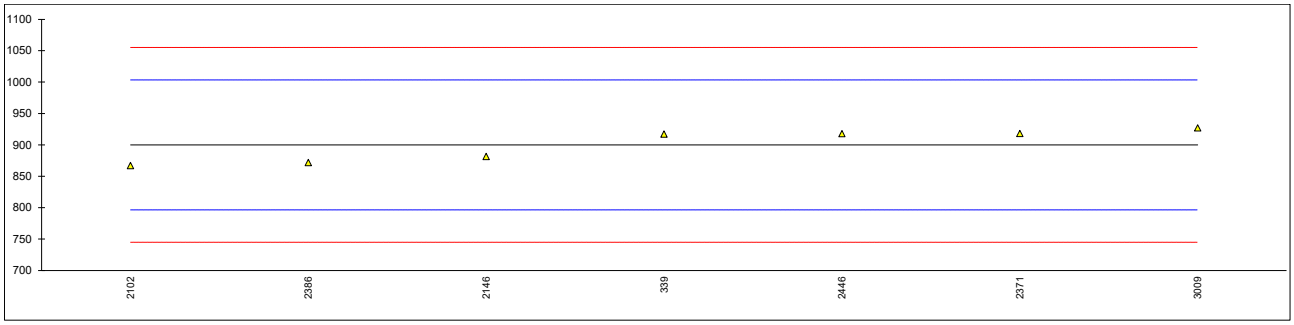
Determination of Formaldehyde in sample #22786; results in mg/kg

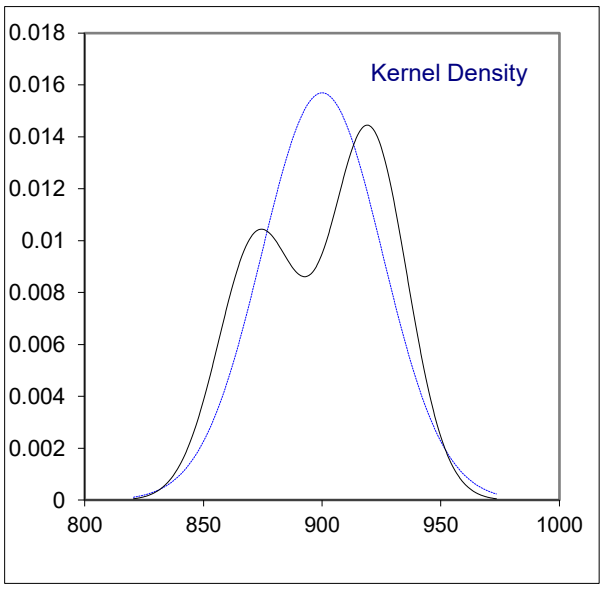
| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 339 | In house | not detected | | ----- | |
| 2102 | In house | Not detected | | ----- | |
| 2146 | | ----- | | ----- | |
| 2278 | | ----- | | ----- | |
| 2371 | TFDA | not determined | | ----- | |
| 2386 | In house | 19 | f+? | ----- | possible false positive test result? |
| 2446 | | ----- | | ----- | |
| 2551 | | ----- | | ----- | |
| 2987 | | ----- | | ----- | |
| 3009 | | not analyzed | | ----- | |
| 3166 | | ----- | | ----- | |
| 3176 | | ----- | | ----- | |

Determination of Benzoic acid CAS No. 65-85-0 in sample #22786; results in mg/kg

| lab | method | value | mark | z(targ) | remarks |
|---|---|---|---|---|---|
| 339 | In house | 917 | | 0.33 | |
| 2102 | In house | 867 | | -0.64 | |
| 2146 | In house | 881.581 | C | -0.36 | First reported: 1342.967 |
| 2278 | | ----- | | ----- | |
| 2371 | TFDA | 918 | | 0.35 | |
| 2386 | In house | 871.8 | | -0.55 | |
| 2446 | In house | 917.776 | | 0.34 | |
| 2551 | | ----- | | ----- | |
| 2987 | | ----- | | ----- | |
| 3009 | In house | 926.9 | | 0.52 | |
| 3166 | | ----- | | ----- | |
| 3176 | | ----- | | ----- | |

| | | |
|---|---|---|
| normality | unknown | |
| n | 7 | |
| outliers | 0 | |
| mean (n) | 900.0082 | |
| st.dev. (n) | 25.41685 | RSD = 2.8% |
| R(calc.) | 71.1672 | |
| st.dev.(Horwitz) | 51.72590 | |
| R(Horwitz) | 144.8325 | |



## APPENDIX 2

### Analytical details for sample #22785

| lab | Accredited acc ISO1725 | Intake amount (g) |
|---|---|---|
| 339 | Yes | 2g |
| 2102 | No | 0.2 gram |
| 2146 | No | 0.5 g |
| 2278 | --- | |
| 2371 | Yes | 5g |
| 2386 | Yes | 2 |
| 2446 | Yes | 0.5g |
| 2551 | Yes | 1 gm |
| 2987 | Yes | |
| 3009 | Yes | 1g |
| 3166 | --- | |
| 3176 | Yes | 1,0 |

### Analytical details for sample #22786

| lab | Accredited acc ISO1725 | Intake amount (g) |
|---|---|---|
| 339 | No | about 4 grams. |
| 2102 | Yes | 1 gram |
| 2146 | No | 0.5 g |
| 2278 | No | 1g |
| 2371 | Yes | 5g |
| 2386 | Yes | 0,6 |
| 2446 | Yes | 0.5 g |
| 2551 | No | 1 gm |
| 2987 | --- | |
| 3009 | Yes | 0.5g |
| 3166 | Yes | 0.5 |
| 3176 | No | 0,15 |

## APPENDIX 3

### Number of participants per country

| | |
|---|---|
| 1 lab in | FINLAND |
| 1 lab in | FRANCE |
| 3 labs in | GERMANY |
| 1 lab in | P.R. of CHINA |
| 1 lab in | SAUDI ARABIA |
| 1 lab in | SWITZERLAND |
| 1 lab in | TAIWAN |
| 1 lab in | THE NETHERLANDS |
| 1 lab in | TURKEY |
| 1 lab in | U.S.A. |

## 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) | = outlier 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 |
| E | = calculation difference between reported test result and result calculated by iis |
| W | = test result withdrawn on request of participant |
| ex | = test result excluded from statistical evaluation |
| n.a. | = not applicable |
| n.e. | = not evaluated |
| n.d. | = not detected |
| fr. | = first reported |
| f+? | = possibly a false positive test result? |
| f-? | = possibly a false negative test result? |

### Literature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