Institute for
Interlaboratory Studies

# Results of Proficiency Test
# PAA from (polyamide) kitchenware
# October 2024



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

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Appendices:

# 1 INTRODUCTION

Some Primary Aromatic Amines (PAA) are considered to be carcinogenic or suspected to be carcinogenic. PAA can be released from food contact materials, like kitchenware such as spoons, due to impurities or breakdown products present in the polyamide. These PAA together with other precursors present in food can form N-Nitrosamines upon ingestion (through metabolic activation), which are potent carcinogens for animals (and most likely also for humans). In 2011 the European Commission issued regulation 284/2011 to lay down specific conditions and detailed procedures for the import of polyamide and melamine kitchenware. In support of this, to enhance harmonization of sampling and its testing, EUR24815: Technical Guidelines on testing the migration of primary aromatic amines from polyamide kitchenware was made public (lit. 13), determining PAA after exposing the kitchenware to acidic test conditions. The limit for PAA is that it should not be present, which means the detection limit applies. In EUR24815 EN2011 it is set as 0.01 mg/kg food or food simulants.

Since 2020 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the determination of PAA from polyamide kitchenware every year. During the annual proficiency testing program of 2024 it was decided to continue the proficiency test for the determination of PAA from polyamide kitchenware.

In this interlaboratory study 23 laboratories in 14 countries registered for participation, see appendix 4 for the number of participants per country. In this report the results of the PAA from polyamide kitchenware proficiency test are presented and discussed.

# 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 a laboratory that has performed the tests in accordance with for ISO/IEC17043 relevant requirements of ISO/IEC17025.
It was decided to send one sample of kitchenware, a spatula with a black nylon part labelled #24725.
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 Organization, Statistics and Evaluation' of October 2024 (iis-protocol, version 4.0). 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 batch of 30 black nylon spatulas containing a relevant concentration of PAA was obtained from a third party. The subsamples were labelled #24725.
The homogeneity of the subsamples was checked by determination of Aniline with an in-house test method on 6 stratified randomly selected subsamples. Migration conditions were: 3% M/V acetic acid and 2 hours at 100 °C, immersion method of migration.

| | Aniline µg/L |
|---|---|
| sample #24725-1 | 20.6 |
| sample #24725-2 | 16.2 |
| sample #24725-3 | 20.9 |
| sample #24725-4 | 20.7 |
| sample #24725-5 | 23.1 |
| sample #24725-6 | 25.1 |

Table 1: homogeneity test results of subsamples #24725

From the above test results the repeatability was calculated and compared with 0.3 times the reproducibility of the reference method in agreement with the procedure of ISO13528, Annex B2 in the next table.

| | Aniline µg/L |
|---|---|
| r (observed) | 8.3 |
| reference method | iis memo 2401 *) |
| 0.3 x R (reference method) | 8.0 |

Table 2: evaluation of the repeatability of subsamples #24725

*) see chapter 4.1 for more information

The calculated repeatability is in agreement with 0.3 times the reproducibility of the reference method. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one polyamide sample labelled #24725 was sent on September 4, 2024.

### 2.5 ANALYZES

The participants were requested to determine 3 different PAA: Aniline (CAS no. 62-53-3), 4,4'-Methylenedianiline (CAS no. 101-77-9) and 2,4-Toluenediamine (CAS no. 95-80-7) using the prescribed test conditions: immersion, first migration step only, simulant 3% M/V acetic acid for 2 hours at 100 °C. In daily practice, not just one item, but more items for testing would have been sent. However, this sample is positive on PAA. This means that one item of the sample is sufficient for the determination of PAA.
It was also requested to report if the laboratory was accredited for the determined components and to report some analytical details.

It was explicitly requested to treat the sample as if it was a routine sample and to report the test results using the indicated units on the report form and not to round the test results, but 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 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 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 appendices 1 and 2 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 appendices 1 and 2. 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 Organization, Statistics and Evaluation' of October 2024 (iis-protocol, version 4.0).
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.

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

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 (derived from e.g. ISO or ASTM test methods), 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 |



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