Institute for
Interlaboratory Studies

Results of Proficiency Test
Bisphenol A EN71-10/11
May 2022

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Toy safety is the practice of ensuring that toys, especially those made for children, are safe, usually through the application of safety standards. In many countries toys must be able to pass safety tests in order to be sold. Many regions model their safety standards on the EU's EN71 standard. In Europe toys must meet the criteria set by the 2009 EC Toy Safety Directive 2009/48/EC, last updated on 05th of June 2022.

Migration of Bisphenol A (BPA) is described in EN 71-9 (Requirements), EN 71-10 (Sample preparation and extraction) and EN 71-11 (Methods of Analysis). The maximum specific limit as described in EN 71-9 is 0.1 mg/L aqueous substrate (or simulant). The European Union has further restricted this limit when it comes to toys. EU directive 2017/898 of 24 May 2017 amending Appendix C to Annex II to Directive 2009/48/EC as regards BPA describes a maximum specific migration limit of 0.04 mg/L aqueous substrate (or simulant). This has been implemented from November 26, 2018 in its member states.

Since 2017 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the determination of migratable Bisphenol A by EN71-10/11 every year. During the annual proficiency testing program 2021/2022 it was decided to continue the proficiency test for the determination of migratable Bisphenol A.

In this interlaboratory study 22 laboratories in 9 countries registered for participation, see appendix 3 for the number of participants per country. In this report the results of the Bisphenol A EN71-10/11 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 piece of white thermal paper labelled #22615 positive on Bisphenol A. Furthermore, a number of test conditions (sample size, simulant, exposure temperature, exposure time and rotation speed) were prescribed.
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 batch of white thermal paper positive on BPA was selected. In total 50 pieces of paper of approximately 5x6cm were cut and wrapped in Aluminum foil and labelled #22615.

The batch was used in a previous proficiency test on Bisphenol A EN71-10/11 as sample #17648 in PT iis17V04. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one sample of thermal paper labelled #22615 was sent on April 27, 2022.

2.5 ANALYZES

The participants were requested to determine Bisphenol A in aqueous migrate using the prescribed test conditions as given in Table 1.

Sample size	cut the sample at width=2cm/length=5cm (surface area is: 2x5=10 cm^2)
Simulant	deionized water
Simulant volume	as per method used
Exposure temperature	20 °C
Exposure time	1 hour
Rotation speed	60 r/min

Table 1: prescribed test conditions for sample #22615

It was also requested to report if the laboratory was accredited for this determination and to report some analytical details. It was advised to keep the thermal paper stored dark, dry and cool and packed until the start of the test. It was also advised not to touch the sample with bare hands.

It was explicitly requested to treat the sample as if it was a routine sample within mind the fixed test conditions mentioned in table 1. Furthermore, it was requested 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 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 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).
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

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 (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

4 EVALUATION

In this proficiency test no problems were encountered with the dispatch of the samples. Four participants reported test results after the final reporting date and one other participant was not able to report any test results.
In total 21 participants reported 21 numerical test results. Observed was one outlying test results, which is 4.8%. In proficiency tests outlier percentages of 3% - 7.5% are quite normal.

The data set proved to have no normal Gaussian distribution and is referred to as “not OK”. The statistical evaluation of this data set should be used with due care, see also paragraph 3.1.

4.1 EVALUATION PER TEST

In this section the reported test results are discussed per test. 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 table together with the original data in appendix 1. The abbreviations, used in this table, are explained in appendix 4.

Test method EN71-11 does mention precision data, unfortunately only at a low level of 0.03 mg BPA/L aqueous migrate. Therefore, the calculated reproducibility was compared against the estimated reproducibility calculated with the Horwitz equation.

Test method EN 71-10 does not describe whether the sample should be used one-sided or two-sided. Therefore, some test conditions like sample size (width=2 cm and length=5 cm) and surface area (2x5=10 cm^2) was prescribed. However, it was also requested to report the sample size (width and length) and the surface area used for the migration. All test results were evaluated as one-sided exposure as the sample is very thin.

BPA in aqueous migrate: 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.

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, the calculated reproducibility (2.8 * standard deviation) and the estimated target reproducibility are presented in the next table.

Component	unit	n	average	2.8 * sd	R(target)
BPA in aqueous migrate	mg/L	20	7.4	3.3	2.5

Table 2: reproducibility on sample #22615

Without further statistical calculations it can be concluded that there is not a good compliance of the group of participants with the reference method.

4.3 COMPARISON OF THE PROFICIENCY TEST OF MAY 2022 WITH PREVIOUS PTS

	May 2022	June 2021	October 2020	December 2019	December 2018
Number of reporting laboratories	21	23	22	31	16
Number of test results	21	23	21	31	30
Number of statistical outliers	1	1	0	6	3
Percentage of statistical outliers	4.8%	4.3%	0.0%	16.2%	9.1%

Table 3: comparison with previous proficiency tests

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

The performance of the determination 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. The uncertainty observed in this PT is in line with previous PTs.

Component	May 2022	June 2021	October 2020	2019-2017	R(target)
BPA in aqueous migrate	16%	16%	29%	8-39%	12-13%

Table 4: development of the uncertainties over the years

4.4 EVALUATION OF THE ANALYTICAL DETAILS

In this PT also some analytical details were asked, the reported details are given in appendix 2. Twelve of the twenty-one participants are ISO/IEC17025 accredited for this test.

All participants except one used 100 mL of simulant. The temperatures used were between 20 and 25 °C, the rotation speed used by all participants was 60 rpm and the time used for the migration was 60 minutes for all participants except one.
Furthermore, it was observed that almost all laboratories used a test portion of 10 cm^2 as surface area by using the prescribed 2x5 cm sample size.

One laboratory reported to have used a surface area of 10 cm^2 and 15 mL of simulant, resulting in a higher surface to volume ratio of 0.7. Because the reported test result for migratable BPA is comparable to the other reported test results, it was decided not to exclude the reported test result from the statistical evaluation.

5 DISCUSSION

All reporting participants were able to detect migratable BPA in sample #22615. The limit stated in EN71-9 is 0.1 mg/L and in directive EU/2017/898 0.04 mg/L. All reporting laboratories would have rejected the sample.

Most likely the variation of the migration test results in real life will be larger than observed in this PT as the test conditions like sample size, simulant, exposure temperature, exposure time and rotation speed will not be prescribed but will be selected by the individual laboratories.

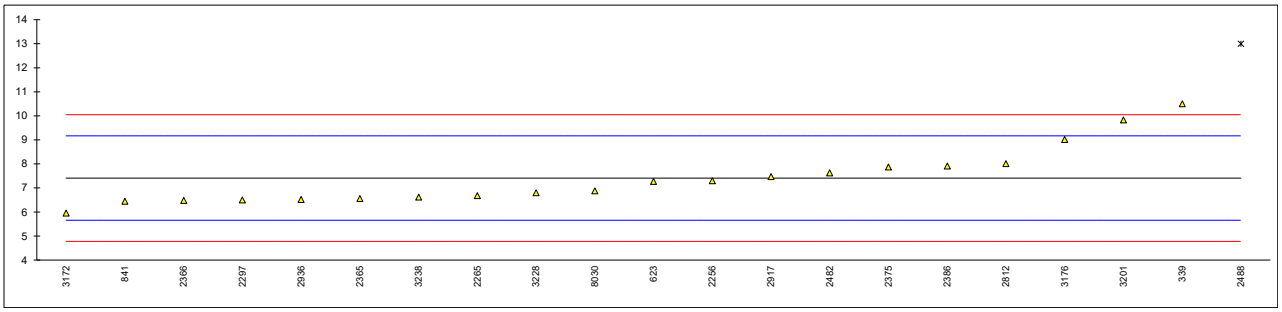
6 CONCLUSION

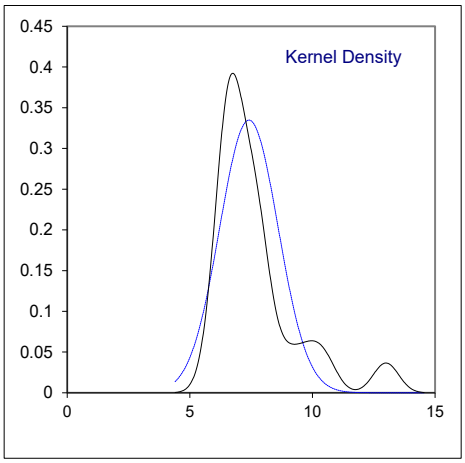
Although it can be concluded that all participants were able to detect migratable BPA in this PT, each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and thus increase of the quality of the analytical results.

APPENDIX 1

Determination of BPA in aqueous migrate on sample #22615; results in mg/L

lab	method	value	mark	z(targ)	remarks
339	In house	10.5		3.52	
623	EN71-11	7.27		-0.16	
841	EN71-11	6.45		-1.10	
2256	EN71-11	7.3007		-0.13	
2265	EN71-11	6.68		-0.84	
2297	EN71-11	6.5		-1.04	
2363		-----		-----	
2365	EN71-11	6.56		-0.97	
2366	EN71-11	6.48		-1.06	
2375	EN71-11	7.87		0.52	
2386	In house	7.909		0.57	
2482	EN71-11	7.63		0.25	
2488	EN71-11	13	C,R(0.01)	6.37	first reported 0.132
2812	EN71-11	8.01	C	0.68	first reported 11967
2917	In house	7.47		0.07	
2936	EN71-11	6.5206		-1.02	
3172	EN71-11	5.955		-1.66	
3176	EN71-11	9.02		1.83	
3201	In house	9.83		2.76	
3228	EN71-11	6.8		-0.70	
3238	EN71-11	6.6165		-0.91	
8030	EN71-11	6.88		-0.61	
	normality	not OK			
	n	20			
	outliers	1			
	mean (n)	7.413			
	st.dev. (n)	1.1912	RSD=16%		
	R(calc.)	3.335			
	st.dev.(Horwitz)	0.8773			
	R(Horwitz)	2.456			





APPENDIX 2 Analytical details

lab	ISO/IEC 17025 accredited	length test portion (cm)	width test portion (cm)	surface area migration (cm^2)	volume simulant migration (mL)	surface to volume ratio calc. by iis	temp. simulant (°C)	rotation speed (r/min)	time used migration (min)
339	No	5	2	10	100	0.1	20	n	60
623	Yes	5	2	10	100	0.1	20	60	60
841	Yes	5	2	10	100	0.1	20	60	60
2256	Yes	5.28	2.08	10.9824	100	0.1	20	60	60
2265	No	---	---	10	100	---	23	60	60
2297	Yes	5.0	2.0	10.0	100	0.1	23	60	60
2363	---	---	---	---	---	---	---	---	---
2365	Yes	5	2	10	100	0.1	20	60	60
2366	Yes	5	2	10	100	0.1	25	60	60
2375	Yes	5	2	10	100	0.1	20	60	60
2386	Yes	5	2	10	100	0.1	20	60	60
2482	No	5	2	10	100	0.1	20	60	60
2488	Yes	5	2	10	100	0.1	24	60	60
2812	No	5	2	10	15	0.7	20	60	0.5
2917	No	5	2	10	100	0.1	20	60	60
2936	No	5	2	10	100	0.1	20	60	60
3172	Yes	5.0	2.0	10.0	100	0.1	25	60	60
3176	No	5.0	2.0	10.0	100.0	0.1	20.0	60.0	60.0
3201	Yes	5	2	10	100	0.1	20	60	60
3228	Yes	5	2	10	100	0.1	22	60	60
3238	No	5	2	10	100	0.1	20	60	60
8030	No	5	2	10	100	0.1	20	60	60

APPENDIX 3

Number of participants per country

2 labs in FRANCE

5 labs in GERMANY

1 lab in INDONESIA

1 lab in ITALY

6 labs in P.R. of CHINA

1 lab in SERBIA

1 lab in THAILAND

4 labs in TURKEY

1 lab in VIETNAM

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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