Institute for
Interlaboratory Studies

Results of Proficiency Test
Bisphenol A EN71-10/11
June 2023

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. 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 2022/2023 it was decided to continue the proficiency test for the determination of migratable Bisphenol A.

In this interlaboratory study 23 laboratories in 10 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 #23635 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 35 pieces of paper of approximately 4 x 5 cm were cut and wrapped in Aluminum foil and labelled #23635.

The batch for sample #23635 was used in a previous proficiency test on Bisphenol A EN71-10/11 as sample #20695 in iis20V06. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one sample of thermal paper labelled #23635 was sent on June 7, 2023.

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 #23635

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. One participant reported test results after the final reporting date.
In total 23 participants reported 23 numerical test results. No outlying test results are observed.

The data set proved to have a normal Gaussian distribution.

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 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 test 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 reference methods are presented in the next table.

Component	unit	n	average	2.8 * sd	R(target)
BPA in aqueous migrate	mg/L	23	7.1	1.8	2.4

Table 2: reproducibility on sample #23635

Without further statistical calculations it can be concluded that there is a good compliance of the group of participants with the reference method.

4.3 COMPARISON OF THE PROFICIENCY TEST OF JUNE 2023 WITH PREVIOUS PTS

	June 2023	May 2022	June 2021	October 2020	December 2019
Number of reporting laboratories	23	21	23	22	31
Number of test results	23	21	23	21	31
Number of statistical outliers	0	1	1	0	6
Percentage of statistical outliers	0.0%	4.8%	4.3%	0.0%	16.2%

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	June 2023	May 2022	June 2021	2020-2017	R(target)
BPA in aqueous migrate	9%	16%	16%	8-39%	12-13%

Table 4: development of the uncertainties over the years

The sample #23635 was used in a previous PT as sample #20695 in iis20V06. The averages found in both PTs for this sample are similar. The calculated reproducibility in this proficiency test has been improved significantly in the 2023 PT compared to the previous PT.

Component	unit	sample #23635			sample #20695		
		n	average	R(calc)	n	average	R(calc)
BPA in aq. migrate	mg/L	23	7.1	1.8	21	7.1	5.7

Table 5: comparison of sample #23635 with #20695

4.4 EVALUATION OF THE ANALYTICAL DETAILS

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

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

For Bisphenol A in aqueous migrate the calculated reproducibility is in agreement with the requirements of the target reproducibility and most of the reported analytical details are similar therefore, no separate statistical analysis has been performed.

5 DISCUSSION

All reporting participants were able to detect migratable BPA in sample #23635. The limit stated in EN71-9 is 0.1 mg/L and in directive EU/2017/898 0.04 mg/L. All reporting participants would have rejected the sample for too much Bisphenol A.

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 are not always prescribed but will be chosen by the individual laboratories.

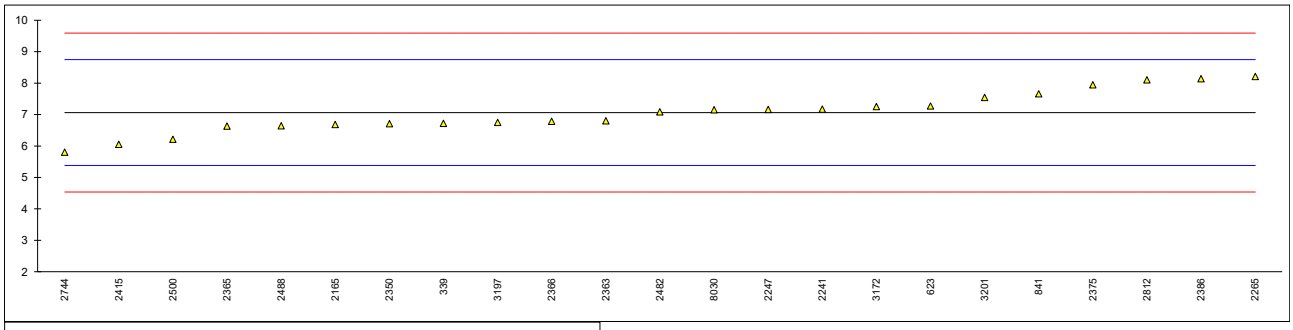
6 CONCLUSION

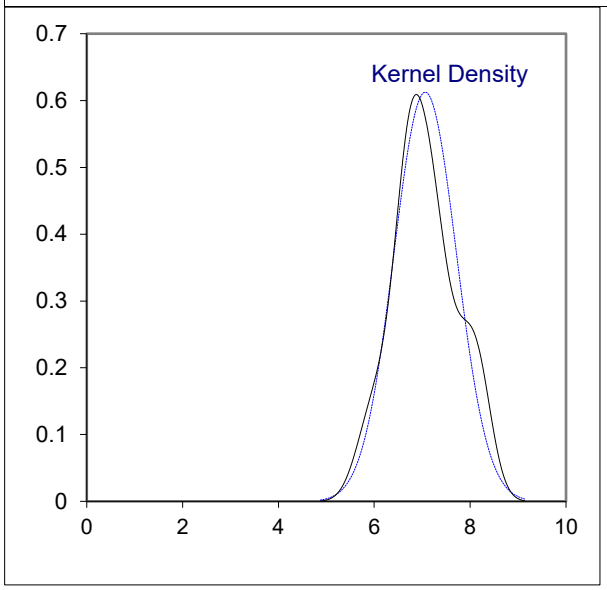
Although it can be concluded that all participants were able to detect migratable BPA in this PT, each participating laboratory will have to evaluate its performance in this study and decide about any corrective actions if necessary. Therefore, participation on a regular basis in this scheme could be 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 #23635; results in mg/L

lab	method	value	mark	z(targ)	remarks
339	In house	6.72		-0.41	
623	EN71-11	7.27		0.25	
841	EN71-11	7.656		0.70	
2165	EN71-11	6.68		-0.45	
2241	EN71-11	7.17		0.13	
2247	EN71-11	7.16		0.12	
2265	EN71-11	8.21		1.36	
2350	EN71-11	6.71		-0.42	
2363	EN71-11	6.8		-0.31	
2365	EN71-11	6.6325		-0.51	
2366	EN71-11	6.78		-0.34	
2375	EN71-11	7.94		1.04	
2386	In house	8.138		1.28	
2415	EN71-11	6.054		-1.20	
2482	EN71-11	7.086		0.03	
2488	EN71-11	6.64		-0.50	
2500	EN71-11	6.21		-1.01	
2744	EN71-11	5.8		-1.50	
2812		8.1		1.23	
3172	EN71-11	7.253		0.23	
3197	EN71-11	6.75		-0.37	
3201	EN71-11	7.54		0.57	
8030	EN71-11	7.15		0.10	
	normality	OK			
	n	23			
	outliers	0			
	mean (n)	7.063			
	st.dev. (n)	0.6517	RSD = 9%		
	R(calc.)	1.825			
	st.dev.(Horwitz)	0.8420			
	R(Horwitz)	2.358			





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 (minutes)
339	No	5	2	10	100	0.1	20	60	60
623	Yes	5	2	10	100	0.1	20	60	60
841	Yes	5.0	2.0	10	100	0.1	21	60	60
2165	Yes	5	2	10	100	0.1	20	60	60
2241	Yes	2	5	10	100	0.1	20	60	60
2247	Yes	5	2	10	100	0.1	20	60	60
2265	Yes	5	2	10	100	0.1	20	60	60
2350	Yes	5	2	10	100	0.1	20	60	60
2363	Yes	5	2	10	100	0.1	20	60	60
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	2	5	26	260	0.1	20	60	60
2415	Yes	5	2	10	100	0.1	20	60	60
2482	No	5	2	10	100	0.1	24.8	18	60
2488	Yes	5	2	10	100	0.1	20	60	60
2500	Yes	5	2	10	100	0.1	20	60	60
2744	Yes	2	5	10	100	0.1	20	60	60
2812	---	-----	-----	-----	-----	-----	-----	-----	-----
3172	Yes	5	2	10	100	0.1	25	60	60
3197	Yes	5	2	10	100	0.1	20	60	60
3201	Yes	5	2	10	100	0.1	20	60	60
8030	No	2	5	10	100	0.1	20	60	60

APPENDIX 3

Number of participants per country

1 lab in FRANCE
4 labs in GERMANY
1 lab in INDIA
1 lab in INDONESIA
1 lab in ITALY
1 lab in KOREA, Republic of
6 labs in P.R. of CHINA
1 lab in THAILAND
5 labs in TURKEY
2 labs 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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