Results of Proficiency Test
Bisphenol-A EN71-10/11
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Organised 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 set 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 (Council Directive 2009/48/EC).
Migration of 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 Bisphenol A 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 2019/2020, it was decided to continue the proficiency test for the determination of migratable Bisphenol-A by EN71-10/11.

In this interlaboratory study, 32 laboratories in 12 different countries registered for participation. See appendix 3 for the number of participants per country. In this report, the test results of the 2019 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 strip of white thermal paper labelled #19666 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 a 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 Bisphenol-A (BPA) was selected. From this batch 50 paperstrips of approximately 2x11 cm were wrapped in Aluminum foil and labelled #19666.
The homogeneity of the subsamples #19666 was checked by the determination of **total** Bisphenol-A content by an in-house method on 10 stratified stratified randomly selected subsamples.

	Total BPA in %M/M
Sample #19666-1	1.13
Sample #19666-2	1.12
Sample #19666-3	1.15
Sample #19666-4	1.13
Sample #19666-5	1.11
Sample #19666-6	1.15
Sample #19666-7	1.13
Sample #19666-8	1.12
Sample #19666-9	1.15
Sample #19666-10	1.14

Table 1: homogeneity test results of subsamples #19666

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

	Total BPA in %M/M
r (observed)	0.04
reference method	Horwitz
0.3 * R (reference method)	0.04

Table 2: evaluation of the repeatability of subsamples #19666

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

To each of the participating laboratories, one sample labelled #19666 containing thermal paper was sent on November 13, 2019.

2.5 ANALYZES

The participants were requested to determine on sample #19666 Bisphenol-A in aqueous simulant using the prescribed test conditions (see table 3).
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.

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 3: prescribed test conditions for sample #19666

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 appropriate 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 reported test results 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.

According to ISO5725 the original test results per determination were submitted to Dixon's, Grubbs' and/or Rosner's outlier tests. Outliers are marked by D(0.01) for the Dixon's test, by G(0.01) or DG(0.01) for the Grubbs' test and by R(0.01) for the Rosner's test. Stragglers are marked by D(0.05) for the Dixon's test, by G(0.05) or DG(0.05) for the Grubbs' test and by R(0.05) for the Rosner's test. Both outliers and stragglers were not included in the calculations of averages and standard deviations.
For each assigned value the uncertainty was determined in accordance with ISO13528. Subsequently the calculated uncertainty was evaluated against the respective requirement based on the target reproducibility in accordance with ISO13528. In this PT, the criterion of ISO13528, paragraph 9.2.1, was met for all evaluated tests, therefore, the uncertainty of all assigned values may be negligible and need not be included in the PT report.

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

3.2 GRAPHICS

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

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

3.3 Z-SCORES

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

The target standard deviation was calculated from the literature reproducibility by division with 2.8. In case no literature reproducibility was available, other target values 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 results is fit-for-use.

The z-scores were calculated in according to:

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

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.
The usual interpretation of z-scores is as follows:

	$\lvert z \rvert$	< 1	good
1 <	$\lvert z \rvert$	< 2	satisfactory
2 <	$\lvert z \rvert$	< 3	questionable
3 <	$\lvert z \rvert$		unsatisfactory

4 EVALUATION

In this interlaboratory study, no problems were encountered with the dispatch of the sample. One participant reported after the final reporting date and one participant did not report any test result. In total 31 participants reported 31 numerical test results. Observed were 6 outlying test results, which is 16.2%. In proficiency studies, outlier percentages of 3% - 7.5% are quite normal.
The original data set proved to have a normal Gaussian distribution.

4.1 EVALUATION PER TEST

In this section the results are discussed per test. The test method, 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 in appendix 1 together with the original data. The abbreviation used in these tables are explained in appendix 4.

Test method EN 71-11 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 reproducibility estimated from 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. Where needed the test results were recalculated to one-sided exposure, see for more discussion paragraph 4.4.

Sample #19666

BPA (migratable): This determination may be problematic. Six statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is almost in agreement with the estimated reproducibility using 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.

Parameter	unit	n	average	2.8 * sd	R (target)
Bisphenol A (migratable)	mg/L	25	7.0	2.7	2.3

Table 4: reproducibility of the test on sample #19666

Without further statistical calculations, it could be concluded that for migration of BPA there is almost a compliance of the group of participating laboratories with the reference method.

4.3 COMPARISON OF THE PROFICIENCY TEST OF DECEMBER 2019 WITH PREVIOUS PTS

The performance of the determinations of the proficiency test was compared, expressed as relative standard deviation (RSD) of the PTs, see table below.

Parameter	December 2019	December 2018	December 2017	R (target)
Bisphenol A (migratable)	14%	34-39%	8.3%	12-13%

Table 5: development of uncertainties over the years

The uncertainty observed in this PT is smaller than the uncertainty observed in the PT conducted in 2018 and is comparable with the uncertainty of the PT conducted in 2017.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

In this PT, also some analytical details were asked (see appendix 2). The majority (61%) of the participants is ISO/IEC17025 accredited for this test. Furthermore, details were requested about the test conditions as described in EN71-10 and 11.

The test methods EN71-10 and EN71-11 describe the extraction and analysis of Organic Chemical Compounds, including the determination of migration of BPA, when 10 cm^2 of a toy or toy material gets into contact with 100 ml water (simulating saliva of a child) for 1 hour at 20°C.
Unfortunately, test method EN 71-10 does not describe if one or both sides should be used in the calculation of the contact surface. It only states to take 10 cm^2 and put it in 100 mL. Other migration tests on for example food contact materials, like EN1186-1 and EN13130-1 do mention 1-sided surface and 2-sided surface. These test methods describe that samples thicker than 0.5 mm are considered to release from both sides, while thinner samples are considered to release as being one side. In this PT the test results were evaluated as one-sided exposure as the sample is very thin (see §4.1).

Almost all participants used 100 mL of simulant, 20°C as temperature, 60 minutes of time and a rotation speed of 60 rpm (see appendix 2).
Further was observed that almost all laboratories used a test portion of 10 cm^2 as surface area of which 21 laboratories used the prescribed 2x5 cm sample size.
Almost all laboratories used 1-sided surface for the determination of migratable BPA. Two laboratories used 2-sided surface, the test results of these two laboratories were converted by iis to 1-sided surface.

5 DISCUSSION

In this proficiency test, the average of the homogeneity test results is not in line with the average (consensus value) from the PT results. There are several reasons for this.

First the test results of the homogeneity are based on the determination of **total** BPA, while the test results of this PT are based on the determination of **migratable** BPA.

Secondly, the goal of homogeneity testing is very different from the goal of the evaluation of the reported PT results. In order to prove the homogeneity of the PT samples, a test method is selected with a high precision (smallest variation). The accuracy (trueness) of the test method is less relevant.

Also, the homogeneity testing is done by one laboratory only. The test results of this (ISO/IEC17025 accredited) laboratory will have a bias (systematic deviation) depending on the test method used. The desire to detect small variations between the PT samples leads to the use of a sensitive test method with high precision, which may be a test method with significant bias.

Finally, each test result reported by the laboratories that participate in the PT will have a bias. However, some will have a positive bias and others a negative bias. These different biases compensate each other in the PT average (consensus value). Therefore, the PT consensus value may deviate from the average of the homogeneity test. At the same time the accuracy of the PT consensus value is more reliable than the accuracy of the average of the results of the homogeneity test.

6 CONCLUSION

All participants did find sample #19666 to be positive on BPA (above the limit of EN71-9 (0.1 mg/L). And almost all participants reported a test value above 0.04 mg/L (above the limit of directive EU/2017/898).

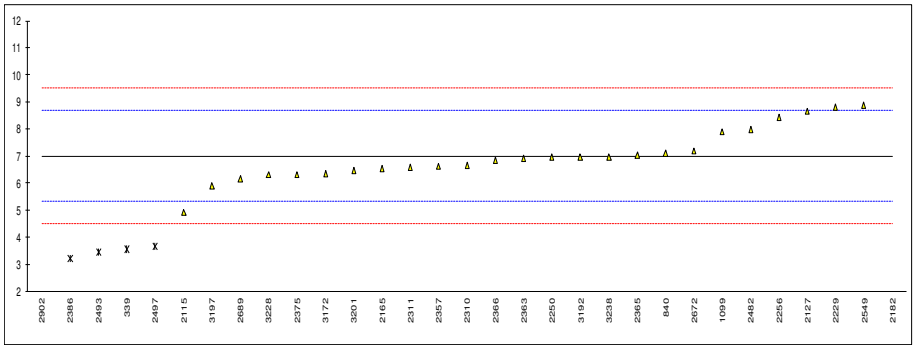
It is to be expected that the variation of the migration test results in real life practise will be larger than observed in this PT as the test conditions like sample size, simulant, exposure temperature, exposure time and rotation speed will not be prescribed but will be selected by the individual laboratories.
Each laboratory has to evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

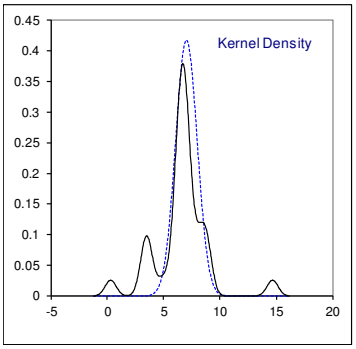
APPENDIX 1

Determination of Migration of BPA on sample #19666; (1-sided surface) results in mg/L

lab	method	value	mark	z(targ)	remarks
339	In house	3.55	R(0.05)	-4.14	
840	EN71-11	7.10		0.10	
1099	EN71-11	7.893		1.05	
2102		-----		-----	
2115	EN71-11	4.9		-2.52	
2127	EN71-11	8.63782		1.94	
2165	EN71-11	6.53		-0.58	
2182	EN71-11	14.67	R(0.01)	9.15	
2229	EN71-11	8.8218		2.16	
2250	EN71-11	6.94	C	-0.09	first reported 0.00694 mg/L
2256	EN71-11	8.436	C	1.70	first reported 10.44
2310	EN71-11	6.67		-0.41	
2311	EN13130-1/13	6.59		-0.51	
2357	EN71-11	6.60		-0.49	
2363	EN71-11	6.9		-0.13	
2365	EN71-11	7.04		0.03	
2366	EN71-11	6.83		-0.22	
2375	EN71-11	6.31		-0.84	
2386	EN71-11	3.227	R(0.05)	-4.52	
2482	EN71-11	7.97		1.14	
2493	EN71-11	3.44	C,R(0.05)	-4.27	reported 1.72 2-sided; converted by iis to 1-sided
2497	EN71-11	3.6538	R(0.05)	-4.01	
2549	EN71-11	8.88	C	2.23	first reported 887.5 mg/L
2672	EN71-11	7.165		0.18	
2689	EN71-11	6.163		-1.02	
2902	EN71-11	0.272	C,R(0.01)	-8.05	first reported 2.72 mg/L
3172	EN71-11	6.36		-0.78	
3192	EN71-11	6.940		-0.09	
3197	EN71-11	5.91		-1.32	
3201	EN71-11	6.462		-0.66	
3228	EN71-11	6.3		-0.85	
3238	EN71-11	6.96776	C	-0.05	reported 3.48388 2-sided; converted by iis to 1-sided

normality	OK	
n	25	
outliers	6	
mean (n)	7.013	RSD = 14%
st.dev. (n)	0.9583	
R(calc.)	2.683	
st.dev.(Horwitz)	0.8369	
R(Horwitz)	2.343	
compare		
R(EN71-11)	0.884	





APPENDIX 2 Analytical details

lab	ISO/IEC17025 accredited?	length test portion (cm)	width test portion (cm)	surface area migration (cm^2)	volume simulant migration (mL)	temp. simulant (°C)	rotation speed (r/min)	time used migration (min)
339	No	2	5	10	100	20	-----	60
840	No	4	2.5	10	100	22	60	60
1099	---	5	2	10	100	20	60	60
2102	---	-----	-----	-----	-----	-----	-----	-----
2115	No	10	1	10	100	20	200	60
2127	Yes	5	2	10	100	20	60	60
2165	Yes	5	2	10	100	20	60	60
2182	Yes	5	2	10	100	20	60	60
2229	Yes	5.0	2.0	10	100	19.8	60	60
2250	Yes	-----	-----	10	100	room temp.	-----	60
2256	Yes	4.0	2.47	9.88	100	20	60	60
2310	Yes	5	2	10	100	25	60	60
2311	Yes	5	2	10	100	20	60	60
2357	---	-----	-----	-----	-----	-----	-----	-----
2363	Yes	5	2	10	100	23	60	60
2365	Yes	5.0	2.0	10.0	100.0	20.4	60.0	60.0
2366	Yes	4	2.5	10	100	22	60	60
2375	No	5	2	10	100	23	60	60
2386	Yes	5	2	10	100	20	60	60
2482	No	5	2	10	100	20	60	60
2493	No	5	2	20	500	22	60	60
2497	No	10	1	10	100	21	60	60
2549	Yes	5	2	10	100	20	60	60
2672	Yes	5.00	2.00	10.00	100.0	21.0	63.0	60.0
2689	Yes	4	2.5	10	100	20	60	60
2902	No	5	2	10	100	20	60	60
3172	Yes	-----	-----	-----	-----	-----	-----	-----
3192	No	5.0	2.0	10.0	100	20	100	60
3197	Yes	5	2	10	100	20	60	60
3201	Yes	5	2	10	100	20	60	60
3228	Yes	5	2	10	100	20	60	60
3238	No	1	5	10	100	20	60	60

APPENDIX 3

Number of participating laboratories per country

2 labs in FRANCE
7 labs in GERMANY
1 lab in HONG KONG
1 lab in HUNGARY
3 labs in INDIA
3 labs in ITALY
9 labs in P.R. of CHINA
1 lab in POLAND
1 lab in SERBIA
1 lab in THE NETHERLANDS
2 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 = possibly an error in calculations
W = test result withdrawn on request of participant
ex = test result excluded from statistical evaluation
n.a. = not applicable
n.d. = not detected
n.e. = not evaluated
fr. = first reported

Literature

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