Institute for
Interlaboratory Studies

Results of Proficiency Test
Migration of elements EN71-3
Category 2
April 2022

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

Author: ing. A. Ouwerkerk
Correctors: ing. R.J. Starink & ing. M. Meijer
Approved by: ing. A.S. Noordman-de Neef

Report: iis22V02B

June 2022

CONTENTS

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, either directly, or through adoption of the ISO8124-3 standard which in itself is modelled on EN71. In Europe, toys must meet the criteria set by the EC Toy Safety Directive 2009/48/EC which applies to toy imports into the EU since 20th of July 2011. There is an exception for the chemical requirements under part III of Annex II of this directive. These chemical requirements came into force on 20th of July 2013.
The test methods EN71-3:19+A1:21 and ISO8124-3:20 both describe the determination of Migration of elements (metals that are considered hazardous) when a toy gets into contact with an acid solution (0.07 n HCl, simulating a gastric acid solution).

Since 2010 the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for Migration of Elements EN71-3 every year. During the annual proficiency testing program 2021/2022 it was decided to continue the proficiency test for the determination of the Migration of Elements. This proficiency test describes the Migration of elements EN71-3 for category 2 samples.

In this interlaboratory study 29 laboratories in 16 countries registered for participation, see appendix 4 for the number of participants per country. In this report the results of the Migration of elements EN71-3 for category 2 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 8 mL fingerpaint labelled #22555.
The participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for statistical evaluation.

2.1 ACCREDITATION

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, is accredited in agreement with ISO/IEC17043:2010 (R007), since January 2000, by the Dutch Accreditation Council (Raad voor Accreditatie). This PT falls under the accredited scope. 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 orange colored fingerpaint was purchased in a local shop. This batch was made positive on the elements Cadmium and Nickel. After mixing thoroughly the batch of fingerpaint was divided over 60 small PE bottles of 10 mL and labelled #22555.
The homogeneity of the subsamples was checked by determination of Cadmium and Nickel in accordance with EN71-3 on 5 stratified randomly selected subsamples.

	Cadmium in mg/kg	Nickel in mg/kg
sample #22555-1	4.112	20.562
sample #22555-2	4.229	20.677
sample #22555-3	4.050	21.503
sample #22555-4	4.297	21.006
sample #22555-5	4.098	20.492

Table 1: homogeneity test results of subsamples #22555

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

	Cadmium in mg/kg	Nickel in mg/kg
r (observed)	0.286	1.164
reference test method	EN71-3:19+A1:21	EN71-3:19+A1:21
0.3 x R (reference test method)	0.698	3.502

Table 2: evaluation of the repeatabilities of subsamples #22555

The calculated repeatabilities are in agreement with 0.3 times the corresponding reproducibility of the reference test method. Therefore, homogeneity of the subsamples was assumed.

To each of the participating laboratories one sample of fingerpaint labelled #22555 was sent on March 02, 2022.

2.5 ANALYZES

The participants were requested to determine the migration of nineteen elements (Aluminum, Antimony, Arsenic, Barium, Boron, Cadmium, Chromium (III), Chromium (VI), Cobalt, Copper, Lead, Manganese, Mercury, Nickel, Selenium, Strontium, Tin, Organic Tin and Zinc) applying the analysis procedure that is routinely used in the laboratory. It was also requested to report if the laboratory was accredited for the determination Migration of Elements 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 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 some problems were encountered with the dispatch of the samples due to COVID-19 pandemic. Therefore, the reporting time on the data entry portal was extended with another week. One participant reported test results after the extended reporting date and two other participants were not able to report any test results. Not all participants were able to report all elements requested.
In total 27 participants reported 72 numerical test results. Observed was 1 outlying test result, which is 1.4%. 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 ELEMENT

In this section the reported test results are discussed per element. 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 5.

EN71-3 method is considered to be the official test method for the determination of elements migrated from different matrices. In 2019 a new version of EN71-3 is published. In 2021 an amended version of the method is published in which the most significant change is the lower limits published in Table 2 for Aluminum.
In test method of EN71-3:19+A1:21 precision data are given in Table 4 and in Table C.1. Table 4 contains precision data from an interlaboratory study. The committee was not able to obtain precision data for all elements for each category via an interlaboratory study. In order to compensate for missing data for certain element and category combinations estimations for the reproducibility have been considered by the committee based on table 4 and input from experts. These precision data are given in table C.1 and are used to evaluate the performance of the group of participants in this PT.

In EN71-3:19+A1:21 a part is introduced that maintaining the pH between 1.1 and 1.3 is very important for the determination of the migration of elements. Therefore, based on the answers given by the participants, the test results of participants who reported pH values outside the range of 1.1 and 1.3 were excluded from the statistical evaluations.

Barium as Ba: This determination was not problematic. No statistical outliers were observed but one test result was excluded. The calculated reproducibility after rejection of the suspect data is in agreement with the requirements of EN71-3:19+A1:21.

Cadmium as Cd: This determination was not problematic. No statistical outliers were observed but one test result was excluded. The calculated reproducibility after rejection of the suspect data is in agreement with the requirements of EN71-3:19+A1:21.

Nickel as Ni: This determination was not problematic. One statistical outlier was observed. The calculated reproducibility after rejection of the statistical outlier is in agreement with the requirements of EN71-3:19+A1:21.

The majority of the participants agreed on a concentration near or below the limit of detection for all other reported elements mentioned in paragraph 2.5. Therefore, no z-scores are calculated for these elements. The reported results can be found in appendix 2.

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.

Element	unit	n	average	2.8 * sd	R(lit)
Barium as Ba	mg/kg	19	15.3	3.7	6.4
Cadmium as Cd	mg/kg	26	3.96	0.79	2.22
Nickel as Ni	mg/kg	24	19.5	4.0	10.9

Table 3: reproducibilities of tests on sample #22555

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

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

	April 2022	April 2021	April 2020	April 2019
Number of reporting laboratories	27	27	36	37
Number of test results	72	94	101	99
Number of statistical outliers	1	5	8	11
Percentage of statistical outliers	1.4%	5.3%	7.9%	11.1%

Table 4: comparison with previous proficiency test

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

The performance of the determinations of the proficiency tests was compared, expressed as relative standard deviation (RSD) of the PTs in the next table.

Element	April 2022	April 2021	April 2020	April 2019	Target
Aluminum	n.e.	n.e.	9%	n.e.	15%
Antimony	n.e.	n.e.	n.e.	n.e.	30%
Arsenic	n.e.	n.e.	n.e.	n.e.	20%
Barium	9%	n.e.	n.e.	22%	15%
Boron	n.e.	9%	n.e.	n.e.	15%
Cadmium	7%	n.e.	6%	n.e.	20%
Chromium (III)	n.e.	25%	n.e.	n.e.	20%
Chromium (VI)	n.e.	n.e.	n.e.	n.e.	50%
Cobalt	n.e.	8%	n.e.	n.e.	20%
Copper	n.e.	n.e.	n.e.	n.e.	15%
Lead	n.e.	n.e.	6%	22%	20%

Element	April 2022	April 2021	April 2020	April 2019	Target
Manganese	n.e.	n.e.	n.e.	n.e.	15%
Mercury	n.e.	n.e.	n.e.	n.e.	30%
Nickel	7%	6%	n.e.	19%	20%
Selenium	n.e.	n.e.	n.e.	n.e.	20%
Strontium	n.e.	n.e.	n.e.	n.e.	15%
Tin	n.e.	n.e.	n.e.	n.e.	20%
Organic Tin	n.e.	n.e.	n.e.	n.e.	50%
Zinc	n.e.	n.e.	n.e.	n.e.	15%

Table 5: development of uncertainties over the years

The uncertainties observed in this PT are lower or equal than the uncertainties observed in previous PTs.

4.4 EVALUATION OF ANALYTICAL DETAILS

Twenty-four of the twenty-seven participants mentioned that they are ISO/IEC17025 accredited for the category 2 determination of Migration of elements EN71-3.
Furthermore, the participants were asked to provide some analytical details which are listed in appendix 3. Based on the answers given the following can be summarized:

- All participants mentioned to have used at least 100 mg or more for sample intake. Please note that test method EN71-3 mentions to take not less than 100 mg whenever possible.
- Twenty-three participants mentioned to have used a volume ratio of 5 mL of HCl solution per 100 mg sample intake for the migration.
- Twenty-three participants have used a solution with a pH between 1.1 and 1.3 (with or without adjustment of HCl solution) for the determination of the elements.

As the majority of the group follow the same analytical procedures no separate statistical analysis has been performed.

5 DISCUSSION

It appeared that EN71-3:19+A1:21 has been followed well by most of the participants. One participant has used a solution with a pH above 1.3 to measure the metals, however the effect on the determination is neglectable.

When the results of this interlaboratory study are compared to the Migration limits from toy materials for category II as mentioned in EN71-3:19+A1:21 (see table below), it was noticed that not all participants would have made identical decisions about the acceptability of the material for the determined components. All reporting laboratories would have rejected sample #22555 for too high level of Cadmium, but for Nickel eighteen laboratories would have rejected the sample while seven laboratories would have accepted the sample.

Element	Category II mg/kg
Aluminum	560
Antimony	11.3
Arsenic	0.9
Barium	375
Boron	300
Cadmium	0.3
Chromium (III)	9.4
Chromium (VI)	0.005
Cobalt	2.6
Copper	156
Lead	0.5
Manganese	300
Mercury	1.9
Nickel	18.8
Selenium	9.4
Strontium	1125
Tin	3750
Organic Tin	0.2
Zinc	938

Table 6: Migration limits from toy materials for Category II as mentioned in EN71-3:19+A1:21

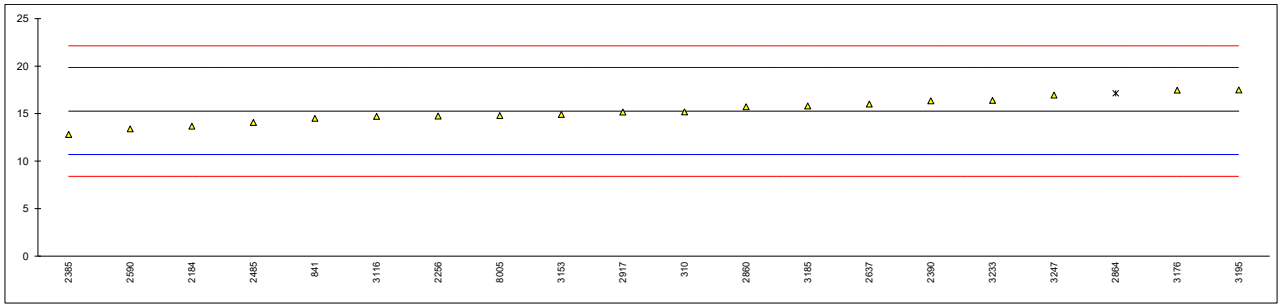
6 CONCLUSION

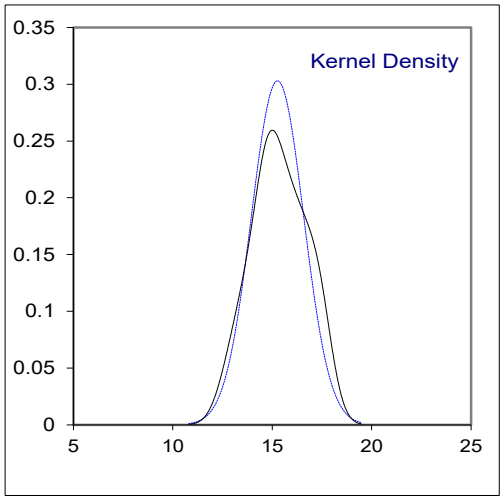
In this PT it appeared that version of EN71-3:19+A1:21 has been followed well by most of the participants. Most of the participants had detected the elements correctly in the samples. Although it can be concluded that most of the participants have no problems with the determination migration of elements in the sample of 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 migration of Barium as Ba on fingerpaint sample #22555; results in mg/kg

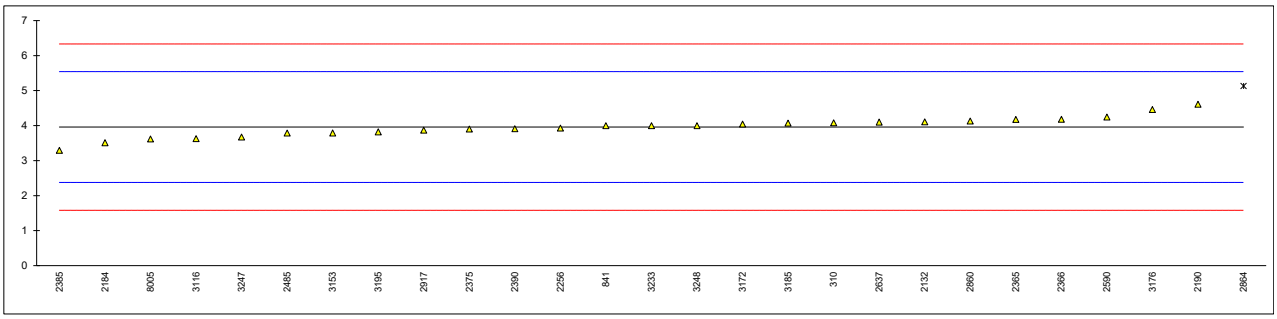
lab	method	value	mark	z(targ)	remarks
310	EN71-3	15.176		-0.04	
551		-----		-----	
841	EN71-3	14.5		-0.34	
2132	EN71-3	<25		-----	
2184	EN71-3	13.68		-0.69	
2190	EN71-3	<50		-----	
2228		-----		-----	
2256	EN71-3	14.75		-0.23	
2365	EN71-3	<50		-----	
2366	EN71-3	<50		-----	
2375	EN71-3	<50		-----	
2385	EN71-3	12.8		-1.08	
2390	EN71-3	16.339		0.47	
2485	EN71-3	14.066		-0.53	
2590	EN71-3	13.394		-0.82	
2637	EN71-3	16		0.32	
2860	In house	15.72		0.20	
2864	EN71-3	17.14	ex	0.82	test result excluded, see §4.1
2917	EN71-3	15.16		-0.05	
3116	EN71-3	14.702		-0.25	
3153	EN71-3	14.91		-0.16	
3172	EN71-3	<50	C	-----	First reported <10
3176	EN71-3	17.46		0.96	
3185	EN71-3	15.82		0.24	
3195	EN71-3	17.5		0.97	
3233	EN71-3	16.39		0.49	
3247	EN71-3	16.95		0.73	
3248		-----		-----	
8005	ASTM F963/GB6675/ISO8124-3	14.794		-0.21	
	normality	OK			
	n	19			
	outliers	0+1ex			
	mean (n)	15.2690			
	st.dev. (n)	1.31630	RSD = 9%		
	R(calc.)	3.6856			
	st.dev.(EN71-3:19+A1:21)	2.29035			
	R(EN71-3:19+A1:21)	6.4130			

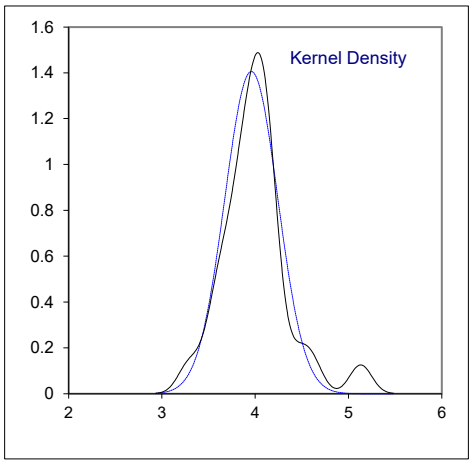




Determination of migration of Cadmium as Cd on fingerpaint sample #22555; results in mg/kg

lab	method	value	mark	z(targ)	remarks
310	EN71-3	4.080		0.15	
551		-----		-----	
841	EN71-3	4.0		0.05	
2132	EN71-3	4.11		0.19	
2184	EN71-3	3.51		-0.57	
2190	EN71-3	4.61		0.82	
2228		-----		-----	
2256	EN71-3	3.93		-0.04	
2365	EN71-3	4.175		0.27	
2366	EN71-3	4.18		0.28	
2375	EN71-3	3.90		-0.07	
2385	EN71-3	3.29		-0.84	
2390	EN71-3	3.909		-0.06	
2485	EN71-3	3.783		-0.22	
2590	EN71-3	4.245		0.36	
2637	EN71-3	4.1		0.18	
2860	In house	4.13		0.22	
2864	EN71-3	5.13	ex	1.48	test result excluded, see §4.1
2917	EN71-3	3.87		-0.11	
3116	EN71-3	3.626		-0.42	
3153	EN71-3	3.79		-0.21	
3172	EN71-3	4.0425		0.11	
3176	EN71-3	4.46		0.63	
3185	EN71-3	4.07		0.14	
3195	EN71-3	3.82		-0.17	
3233	EN71-3	4.00		0.05	
3247	EN71-3	3.67		-0.36	
3248	EN71-3	4.0		0.05	
8005	ASTM F963/GB6675/ISO8124-3	3.620		-0.43	
	normality	OK			
	n	26			
	outliers	0+1ex			
	mean (n)	3.9585			
	st.dev. (n)	0.28391	RSD = 7%		
	R(calc.)	0.7949			
	st.dev.(EN71-3:19+A1:21)	0.79170			
	R(EN71-3:19+A1:21)	2.2167			

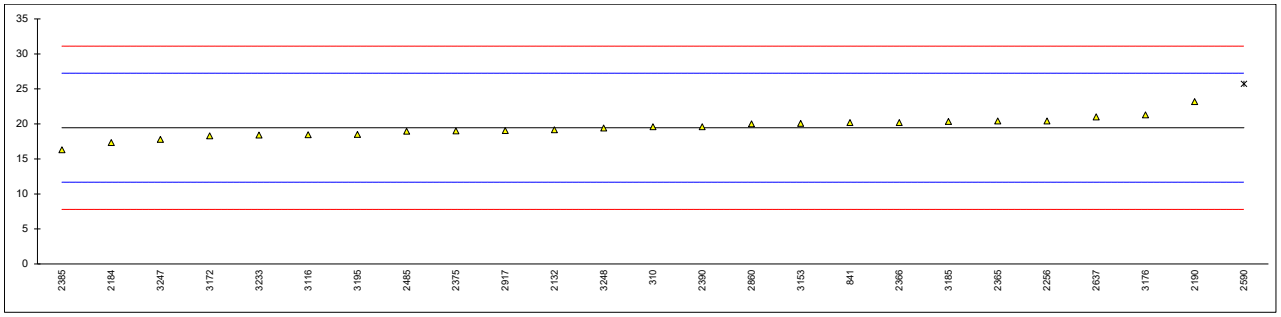


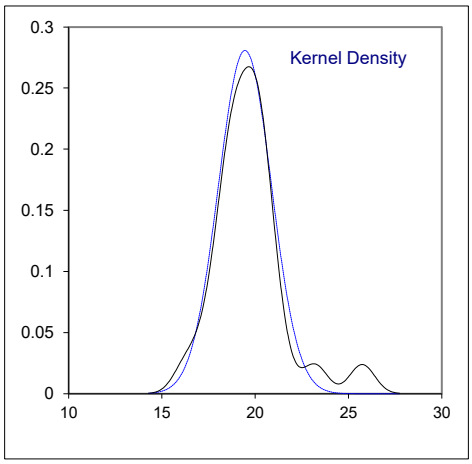


Determination of migration of Nickel as Ni on fingerpaint sample #22555; results in mg/kg

lab	method	value	mark	z(targ)	remarks
310	EN71-3	19.591		0.03	
551		-----		-----	
841	EN71-3	20.2		0.19	
2132	EN71-3	19.16		-0.08	
2184	EN71-3	17.33		-0.55	
2190	EN71-3	23.19		0.96	
2228		-----		-----	
2256	EN71-3	20.42		0.25	
2365	EN71-3	20.41		0.24	
2366	EN71-3	20.2		0.19	
2375	EN71-3	19		-0.12	
2385	EN71-3	16.3		-0.81	
2390	EN71-3	19.597		0.04	
2485	EN71-3	18.959		-0.13	
2590	EN71-3	25.734	R(0.01)	1.61	
2637	EN71-3	21		0.40	
2860	In house	20.02		0.14	
2864		-----		-----	
2917	EN71-3	19.04		-0.11	
3116	EN71-3	18.466		-0.25	
3153	EN71-3	20.07		0.16	
3172	EN71-3	18.30		-0.30	
3176	EN71-3	21.28		0.47	
3185	EN71-3	20.36		0.23	
3195	EN71-3	18.5		-0.25	
3233	EN71-3	18.39		-0.27	
3247	EN71-3	17.80		-0.43	
3248	EN71-3	19.4		-0.01	
8005		-----		-----	

	normality	suspect
	n	24
	outliers	1
	mean (n)	19.4576
	st.dev. (n)	1.42124
	R(calc.)	3.9795
	st.dev.(EN71-3:19+A1:21)	3.89153
	R(EN71-3:19+A1:21)	10.8963





APPENDIX 2

Determination of migration of other elements on sample #22555; results in mg/kg

lab	Al	Sb	As	B	Cr (III)	Cr(VI)	Co	Cu
310	1.349	0.247	<0.5	<50	<1.0	<0.005	<0.5	<50
551	n	n	n	n	n	n	n	n
841	<2.5	<0.1	<0.1	<2.5	0.058	<0.002	<0.1	<2.5
2132	<50	<1	<0.05	<25	<1	<0.0035	<0.1	<15
2184	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2190	<50	<5	<0.5	<50	<5	nd	<1	<50
2228	n	n	n	n	n	n	n	n
2256	not detected	not detected	not detected	not detected	0.054	not detected	not detected	6.54
2365	<50	<1	<0.4	<50	<1	<0.0025	<0.5	<50
2366	<50	<1	<0.4	<50	<1	<0.0025	<0.5	<50
2375	<50	<1	<0.4	<50	<1	<0.0025	<0.5	<50
2385	<10	<1	<1	<1	<0.5	<0.02	<0.5	<5
2390	Not Detected	Not Detected	Not Detected	Not Detected	0.351	Not Detected	Not Detected	Not Detected
2485	n	n	n	n	n	n	n	n
2590	4.450	< L.O.Q.	< L.O.Q.	n	< L.O.Q.	n	< L.O.Q.	< L.O.Q.
2637	0.8	<0,1	<0,1	<1	<0,5	<0,1	<0,1	<0,5
2860	<0,50	<0,50	<0,25	<0,50	<0,50	n	<0,50	<0,50
2864	n	not detected	not detected	n	n	n	n	n
2917	<0.25	<0.25	<0.25	<0.25	<0.25	n	<0.25	<0.25
3116	<2	<2	<0.15	<5	<1	<0.002	<2	<2
3153	<100	<1	<0.3	<50	<1	<0.0025	<1	<10
3172	< 50	< 2	< 0.1	< 50	< 2	< 0.005	< 1	< 50
3176	4.74	0.37	n	3.53	n	n	n	0.60
3185	<100	<1	<0.5	<50	<1	<0.0025	<1	<10
3195	23.0	<0,50	<0,20	53.5	n	n	<0,10	<1,0
3233	< 5	< 5	< 0.05	< 5	0.12	< 0.0025	< 0.5	< 5
3247	5.68	not detected	not detected	not detected	not detected	n	not detected	not detected
3248	<10	<1	<0.45	<100	<1	<0.0025	<1	<10
8005	n	<2	<2	n	n	n	n	n

lab	Pb	Mn	Hg	Se	Sr	Sn	Org Sn	Zn
310	<0.5	<50	0.473	<5	0.254	<0.08	n	0.483
551	n	n	n	n	n	n	n	n
841	<0.1	<2.5	<0.1	<0.5	<2.5	<0.025	<0.04	<2.5
2132	<0.1	<25	<0.1	<1	<50	<10	N/A	<50
2184	not detected	not detected	not detected	not detected	not detected	not detected	not detected	not detected
2190	<0.5	<50	<1	<5	<50	<4	nd	<50
2228	n	n	n	n	n	n	n	n
2256	0.38	not detected	0.074	not detected	not detected	not detected	not detected	13.68
2365	<0.2	<50	<0.5	<4	<50	<0.08	n	<50
2366	<0.2	<50	<0.5	<4	<50	<0.03	<0.03	<50
2375	<0.2	<50	<0.5	<4	<50	<0.08	n	<50
2385	<1	<1	0.15	<1	<5	<1	<0.2	<5
2390	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected	Not Detected
2485	n	n	0.162	n	0.156	n	n	n
2590	< L.O.Q.	< L.O.Q.	< L.O.Q.	< L.O.Q.	< L.O.Q.	< L.O.Q.	n	53.800
2637	<0,1	<0,5	0.11	<1	0.2	<0,5	n	2
2860	<0,25	<0,50	0.72	<0,50	<0,50	<0,50	n	<0,50
2864	not detected	n	not detected	not detected	n	n	n	n
2917	<0.25	<0.25	<0.25	<0.5	<0.5	<0.25	n	4.58
3116	<0.2	<2	<0.15	<2	<2	<2	<0.0164	<5
3153	<0.1	<10	<0.5	<1	<100	<10	<0.1	<100
3172	< 0.3	< 50	< 0.5	< 1	< 50	< 50	< 0.05	< 50
3176	0.26	0.42	0.15	n	0.54	n	n	5.65
3185	<0.1	<10	<1	<1	<100	<0.05	<0.15	<100
3195	<0,50	<1,0	0.229	<0,50	<5,0	<0,10	n	<5,0
3233	0.38	< 5	< 0.5	< 5	< 5	< 0.05	< 0.04	8.48
3247	0.95	not detected	not detected	not detected	not detected	not detected	n	1.20
3248	<0.25	<10	<0.95	<1	<10	<0.8	<0.2	<10
8005	<2	n	<2	<2	n	n	n	n

APPENDIX 3 Analytical details

lab	ISO/IEC17025 accredited	Sample intake (g)	Amount of 0.07 mol/L HCl solution used (mL)	pH after shaking	pH adjusted after shaking?	pH after adjustment
310	Yes	0.2401	12	1.5	Yes	1.2
551	---				---	
841	Yes	0.5 grams	25 ml	<1.3	Yes	<1.3
2132	Yes	0.1009 gram	5 mL	1.21	No	
2184	Yes	0.1g	5ml	1.36	Yes	1.17
2190	Yes	0.2	10ml	1.19	---	
2228	---				---	
2256	Yes	0.2149	10.7	1.256	No	N/A
2365	Yes	0.4g	20mL	1.19	No	
2366	Yes	0.2	10	1.27	No	NA
2375	Yes				---	
2385	Yes	~ 0.5 g	25 mL	1.182	No	
2390	Yes	0.4988g	25ml	1.2	No	
2485	No	0.1 grams	5 mL	1.25	No	
2590	Yes	0.1	10	1.65	Yes	1.16
2637	Yes	0,4	20 ml		---	
2860	Yes	0,4100	20,5	1,11	No	/
2864	Yes	100 mg	5 mL	1.4	No	
2917	Yes	0.4208 and 0.8809	20.1 AND 40.2	1.3 and 1.3	Yes	1.1 and 1.1
3116	Yes	0.25 grams	12.5	1.1 - 1.2	No	Not applicable
3153	Yes	0.2 gram	10 mL	1.20	No	1.20
3172	Yes				---	
3176	Yes	0,05	50	1,27	No	
3185	Yes	0.2g	10mL	1.24	No	1.24
3195	No	0,20g	10mL	2,0	Yes	1,1
3233	Yes	0.1144 g	5.7 mL	1.23	No	
3247	No	0.2g	10ml	1-1.5	No	
3248	Yes	0.2000g	10mL	1.31	Yes	1.22
8005	Yes	0.25g	12.5	1.34	Yes	1.1-1.2

APPENDIX 4

Number of participants per country

1 lab in	BRAZIL
1 lab in	CYPRUS
2 labs in	FRANCE
3 labs in	GERMANY
6 labs in	HONG KONG
2 labs in	ITALY
1 lab in	MEXICO
4 labs in	P.R. of CHINA
1 lab in	PAKISTAN
1 lab in	SERBIA
1 lab in	SLOVENIA
1 lab in	SWITZERLAND
1 lab in	TAIWAN
1 lab in	THE NETHERLANDS
2 labs in	TURKEY
1 lab in	VIETNAM

APPENDIX 5

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

1 iis Interlaboratory Studies, Protocol for the Organisation, Statistics & Evaluation, June 2018
2 ISO5725:86
3 ISO5725 parts 1-6:94
4 ISO13528:05
5 M. Thompson and R. Wood, J. AOAC Int, 76, 926, (1993)
6 W.J. Youden and E.H. Steiner, Statistical Manual of the AOAC, (1975)
7 P.L. Davies, Fr. Z. Anal. Chem, 331, 513, (1988)
8 J.N. Miller, Analyst, 118, 455, (1993)
9 Analytical Methods Committee, Technical Brief, No 4, January 2001
10 P.J. Lowthian and M. Thompson, The Royal Society of Chemistry, Analyst, 127, 1359-1364, (2002)
11 W. Horwitz and R. Albert, J. AOAC Int, 79.3, 589-621, (1996)
12 Bernard Rosner, Percentage Points for a Generalized ESD Many-Outlier Procedure, Technometrics, 25(2), 165-172, (1983)