Results of Proficiency Test
AZO Dyes in Finger Paint
June 2021

Organized by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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1 INTRODUCTION

Some Azo Dyes are known to metabolise in aromatic amines. These primary aromatic amines have been considered mutagenic and/or carcinogenic for many years. Fingerpaint is especially important as a matrix to avoid Azo colorants that break down to aromatic amines, because fingerpaint is mainly used by children, with direct skin contact and possibility of ingestion of the paint. Method EN71-7 Finger Paints - Requirements and test methods describes a limit of 10 mg/kg of every primary aromatic amine present and a limit of 20 mg/kg for the total of primary aromatic amines.

In 2020 the Institute for Interlaboratory Studies (iis) organized a proficiency scheme for the analysis of AZO Dyes in Finger Paint for the first time. During the annual proficiency testing program 2020/2021 it was decided to continue the proficiency test for the analysis of AZO Dyes in Finger Paint.

In this interlaboratory study 9 laboratories in 7 different countries registered for participation. See appendix 4 for the number of participants per country. In this report the results of the AZO Dyes in Finger Paint 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 finger paint in a 10mL bottle labelled #21615, positive on banned Aromatic Amines derived from AZO dyes.
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 blue finger paint was obtained from a local supplier and made positive on 3,3'-Dimethylbenzidine with Acid Red 114, resulting in a blue/purple colored finger paint. After homogenization the batch was divided over 30 bottles of 10mL and labelled #21615. The homogeneity of the subsamples was checked by determination of 3,3'-Dimethylbenzidine in accordance with ISO14362 on 4 stratified randomly selected subsamples.

	3,3'-Dimethylbenzidine in mg/kg
sample #21615-1	271.6
sample #21615-2	251.1
sample #21615-3	247.7
sample #21615-4	250.2

Table 1: homogeneity test results of subsamples #21615

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

	3,3'-Dimethylbenzidine in mg/kg
r (observed)	30.9
reference test method	ISO14362-1:17
0.3 x R (reference test method)	34.7

Table 2: evaluation of the repeatability of subsamples #21615

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

To each of the participating laboratories one sample of finger paint labelled #21615 was sent on May 19, 2021.

2.5 ANALYZES

The participants were requested to determine the concentrations of the aromatic amines:

Benzidine (CAS No. 92-87-5)
2-Naphtylamine (CAS No. 91-59-8)
4-Chloro-2-methyl-aniline (CAS No. 95-69-2)
4-Aminodiphenyl (CAS No. 92-67-1)
o-Aminoazotoluene (CAS No. 97-56-3)
2-Amino-4-nitro-toluene (CAS No. 99-55-8)
4-Chloroaniline (CAS No. 106-47-8)
2,4-Diaminoanisole (CAS No. 615-05-4)
4,4'-Diaminodiphenylmethane (CAS No. 101-77-9)
3,3'-Dichlorobenzidine (CAS No. 91-94-1)
3,3'-Dimethoxybenzidine (CAS No. 119-90-4)
3,3'-Dimethylbenzidine (CAS No. 119-93-7)
3,3'-Dimethyl-4,4'-diaminodiphenyl methane (CAS No. 838-88-0)
p-Cresidine (CAS No. 120-71-8)
2,2'-Dichloro-4,4'-methylenedianiline (CAS No. 101-14-4)
4,4'-Oxydianiline (CAS No. 101-80-4)
4,4'-Thiodianiline (CAS No. 139-65-1)
o-Toluidine (CAS No. 95-53-4)
2,4-Xylidine (CAS No. 95-68-1)
2,6-Xylidine (CAS No. 87-62-7)
4-Amino-3-fluorophenol (CAS No. 399-95-1)
6-Amino-2-ethoxynaphthalene (CAS No. 293733-21-8)
2-Methoxyaniline or o-Anisidine (CAS No. 90-04-0)
4-Aminoazobenzene (CAS No. 60-09-3)
4-Methyl-m-phenylenediamine (CAS No. 95.80-7)
2,4,5-Trimethylaniline (CAS No. 137-17-7)
Aniline (CAS No. 62-53-3)

It was also requested to report if the laboratory was accredited to determine the reported components and to report some analytical details.

It was explicitly requested to treat the sample as if it was a routine sample and to report the test results using the indicated units on the report form and not to round the test results, but report as much significant figures as possible. It was also requested not to report 'less than' test results, which are above the detection limit, because such test results cannot be used for meaningful statistical evaluations.

To get comparable test results a detailed report form and a letter of instructions are prepared. On the report form the reporting units are given as well as the reference test methods (when applicable) that will be used during the evaluation. The detailed report form and the letter of instructions are both made available on the data entry portal www.kpmd.co.uk/sgs-iis-cts/. The participating laboratories are also requested to confirm the sample receipt on this data entry portal. The letter of instructions can also be downloaded from the iis website www.iisnl.com.

3 RESULTS

During five weeks after sample dispatch, the test results of the individual laboratories were gathered via the data entry portal www.kpmd.co.uk/sgs-iis/. The reported test results are tabulated per determination in appendix 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 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 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, e.g. ISO reproducibilities, 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. In some cases, a reproducibility based on former iis proficiency tests could be used.

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:

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

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. 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 and one other participant was not able to report any test results. Not all laboratories were able to report all components requested.
In total 8 participants reported 8 numerical test results. Observed was 1 outlying test result.

The data set proved not to have a normal Gaussian distribution. This is referred to as “not OK” or “suspect”. The statistical evaluation of this data set should be used with due care, see also paragraph 3.1.

4.1 EVALUATION PER COMPONENT

In this section the reported test results are discussed per component. 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. The abbreviations, used in these tables, are explained in appendix 5.

Allmost all reporting participants used test method EN71-7. Unfortunately, this method only states a precision for 3,3’-Dimethylbenzidine with data from two laboratories (a mean and an uncertainty) at a concentration of 1 mg/kg. This is a much lower than the concentration found in this PT and not representative for this concentration. However, ISO14362-1:17 does have a precision statement for aromatic amines in Annex B, Table B.2 for concentrations around 25 mg/kg. This is a method for testing Azo Dyes in textile, but the determination of the Aromatic Amines in the solution will be similar. Therefore, the precision of this method may also apply to this PT. Regretfully, not for all listed Aromatic Amines precision data are available, but for the component 3,3’-Dimethylbenzidine, which is present in sample #21615 a precision statement is mentioned.

3,3'-Dimethylbenzidine: The 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 ISO14362-1:2017.

The majority of the participants agreed on a concentration near or below the limit of detection for all other aromatic amines mentioned in paragraph 2.5. Therefore, no z-scores are calculated for these aromatic amines. The test results of these components are given in appendix 2.

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibilities 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 reproducibilities (2.8 * standard deviation) and the target reproducibility derived from literature reference test methods (in casu ISO test method) are presented in the next table.

Component	unit	n	average	2.8 * sd	R(lit)
3,3'-Dimethylbenzidine	mg/kg	7	104.3	43.7	51.2

Table 3: reproducibility on sample #21615

Without further statistical calculations, it can be concluded that for 3,3'-Dimethylbenzidine there is a good compliance of the group of participants with the reference test method.

4.3 COMPARISON OF THE PROFICIENCY TEST OF JUNE 2021 WITH PREVIOUS PT

	June 2021	June 2020
Number of reporting laboratories	8	5
Number of test results	8	5
Number of statistical outliers	1	0

Table 4: comparison with previous proficiency tests

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

Component	June 2021	June 2020	Target
3,3'-Dimethoxybenzidine	n.e.	4%	13%
3,3'-Dimethylbenzidine	15%	n.e.	18%

Table 5: development of uncertainties of Azo Dyes in finger paint over the years

The uncertainty for 3,3'-Dimethylbenzidine in this PT is good in line with the target uncertainty.

4.4 EVALUATION ANALYTICAL DETAILS

The participants were asked to provide some analytical details which are listed in appendix 3. Based on the answers the following can be summarized:

- almost all mentioned (n=7 out of 8) that they are ISO/IEC17025 accredited to determine the reported components.
- two out of eight participants mentioned to have used 0.1 grams of sample intake, three used 0.5 grams and three used 1 gram.
- only two participants mentioned a pH value of the finger paint when tested, they reported a value between pH 6 and 7

As the majority of the group is reporting to have used the same conditions, no conclusions could be drawn form these analytical details.

5 DISCUSSION

All reporting participants were able to detect 3,3'-Dimethylbenzidine in the sample. No other aromatic amines were detected.
The PT sample was well above the limit of 10 mg/kg for a single aromatic amine as mentioned in EN71-7. All participants would reject this sample for too much banned aromatic amines.

In this PT 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 goal of the 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.
Secondly, the homogeneity testing is done by one laboratory only. The test results of this (ISO/IEC 17025 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.
Also 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.

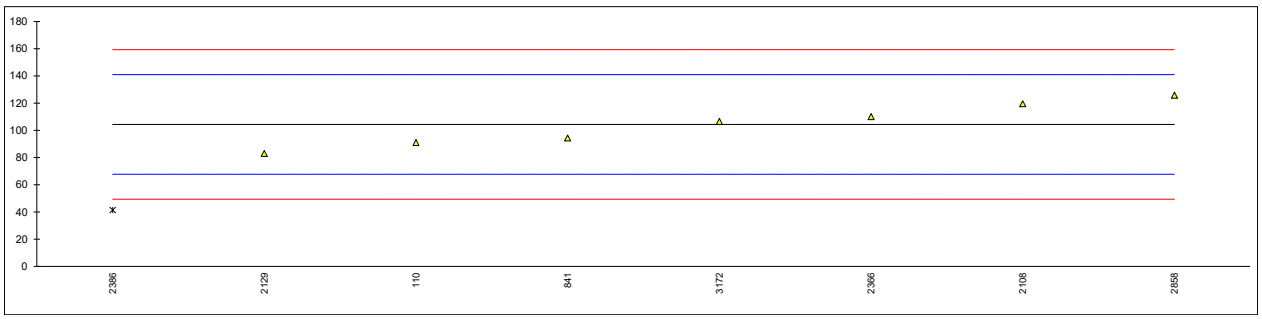
6 CONCLUSION

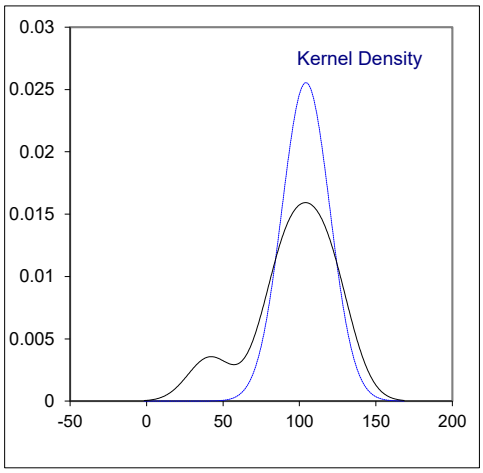
Each laboratory should evaluate its performance in this study and make decisions about necessary corrective actions. Therefore, participation on a regular basis in this scheme could be helpful to improve the performance and the quality of the analytical results.

APPENDIX 1

Determination of 3,3'-Dimethylbenzidine (CAS no. 119-93-7) in sample #21615; results in mg/kg

lab	method	value	mark	z(targ)	remarks
110	-----	91		-0.73	
841	In house	94.4		-0.54	
2102	-----	-----		-----	
2108	EN71-7	119.5379		0.83	
2129	EN71-7	82.94		-1.17	
2366	EN71-7	110		0.31	
2386	EN71-7	41.4	D(0.05)	-3.44	
2858	In house	125.81		1.17	
3172	EN71-7	106.546		0.12	
	normality	unknown			
	n	7			
	outliers	1			
	mean (n)	104.319			
	st.dev. (n)	15.6181	RSD = 15%		
	R(calc.)	43.731			
	st.dev.(ISO14362-1:17)	18.2931			
	R(ISO14362-1:17)	51.221			





APPENDIX 2 Other reported aromatic amines

Abbreviations

BD = Benzidine (CAS no. 92-87-5)
2NA = 2-Naphtylamine (CAS no. 91-59-8)
4CoT = 4-Chloro-o-toluidine / 4-Chloro-2-methyl-aniline (CAS no. 95-69-2)
4AD = 4-Aminodiphenyl (CAS no. 92-67-1)
oAAT = o-Aminoazotoluene (CAS no. 97-56-3)
ANT = 2-Amino-4-nitro-toluene (CAS no. 99-55-8)
4CA = 4-Chloroaniline (CAS no. 106-47-8)
DAA = 2,4-Diaminoanisole (CAS no. 615-05-4)
DADM = 4,4'-Diaminodiphenylmethane (CAS no. 101-77-9)
DCB = 3,3'-Dichlorobenzidine (CAS no. 91-94-1)
DMoxB = 3,3'-Dimethoxybenzidine (CAS no. 119-90-4)
DDDM = 3,3'-Dimethyl-4,4'-diaminodiphenyl methane (CAS no. 838-88-0)
pC = p-Cresidine (CAS no. 120-71-8)
DMD = 2,2'-Dichloro-4,4'-methylenedianiline (CAS no. 101-14-4)
OA = 4,4'-Oxydianiline (CAS no. 101-80-4)
TA = 4,4'-Thiodianiline (CAS no. 139-65-1)
oT = o-Toluidine (CAS no. 95-53-4)
24X = 2,4-Xylidine (CAS no. 95-68-1)
26X = 2,6-Xylidine (CAS no. 87-62-7)
AFP = 4-Amino-3-fluorophenol (CAS no. 399-95-1)
AEN = 6-Amino-2-ethoxynaphthalene (CAS no. 293733-21-8)
2MA = 2-Methoxyaniline (CAS no. 90-04-0)
4AAB = 4-Aminoazobenzene (CAS no. 60-09-3)
4MPD = 4-Methyl-m-phenylenediamine (CAS no. 95-80-7)
TMA = 2,4,5-Trimethylaniline (CAS no. 137-17-7)
AL = Aniline (CAS no. 62-53-3)

Sample #21615; abbreviations explained above

lab	BD	2NA	4CoT	4AD	oAAT	ANT	4CA	DAA	DADM	DCB	DMoxB	DDDM	pC
110	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
841	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
2102	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
2108	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
2129	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
2366	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
2386	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
2858	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
3172	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

Sample #21615 - continued; abbreviations explained above

lab	DMD	OA	TA	oT	24X	26X	AFP	AEN	2MA	4AAB	4MPD	TMA	AL
110	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
841	<5	<5	<5	<5	<5	<5	No capabilities	No capabilities	<5	<5	<5	<5	<5
2102	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
2108	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
2129	<5	<5	<5	<5	<5	<5	<5	-----	<5	<5	<5	<5	<5
2366	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
2386	<5	<5	<5	<5	<5	<5	not determind	<5	<5	<5	<5	<5	<5
2858	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
3172	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5	< 5

APPENDIX 3 Analytical details

lab	ISO/IEC17025 accredited	sample intake (g)	pH of fingerpaint	remarks
110	Yes	.5	no	
841	No	1 grams	-----	4-Amino-3-fluorophenol, CAS No. 399-95-1 and 6-Amino-2-ethoxynaphthalene, CAS No. 293733-21-8 is not in our capabilites
2102	-----	-----	-----	
2108	Yes	0,1 g	not measured	
2129	Yes	0.5	no	it is hard to handle to weigh an alliquot because of the consistancy/viscosity.
2366	Yes	1g	-----	
2386	Yes	0.5	pH 6	
2858	Yes	0.1 gm	6.7	
3172	Yes	1	-----	

APPENDIX 4

Number of participants per country

1 lab in	BANGLADESH
3 labs in	GERMANY
1 lab in	ITALY
1 lab in	P.R. of CHINA
1 lab in	THE NETHERLANDS
1 lab in	U.S.A.
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

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