Results of Proficiency Test
Nickel Release
May 2018

Organised by: Institute for Interlaboratory Studies
Spijkenisse, the Netherlands

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Report: iis18V03

September 2018

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1 INTRODUCTION

Nickel has always been used in various applications, as a pure metal, as a plated substance on another metal or as an alloy. Nickel applications usually do not give problems, but when Nickel comes into prolonged and direct contact with the human skin, sensitization can occur. When a person becomes sensitive to Nickel, even the smallest amounts can provoke an allergic reaction. By this, Nickel is the most frequent cause of contact allergy in Europe. Both the contact itself (sometimes enhanced by damaged skin) and skin conditions as sweat can cause the body to be exposed to Nickel. In order to decrease the amount of people that become sensitized, Nickel containing items that are used in prolonged human contact are tested for Nickel release. These products involve products like jewellery in piercings (ear rings), other jewellery, watches or clothes fasteners, such as buttons and belts.

Since 2014, the Institute for Interlaboratory Studies (iis) organizes a proficiency scheme for the determination of Nickel release every year. During the annual proficiency testing program 2017/2018, it was decided to continue the proficiency test for the analysis of Nickel release. In this interlaboratory study 114 laboratories in 27 different countries registered for participation. See appendix 5 for the number of participants per country. In this report, the test results of the 2018 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 organiser of this proficiency test (PT). Sample analyses for fit-for-use and homogeneity testing were subcontracted to an ISO/IEC 17025 accredited laboratory. It was decided to send three pieces of one non-coated sample (labelled #18575), positive on Nickel release and a metallic leaf (a piece of an earring) (labelled #18576) for surface determination only. The participants were requested to report rounded and unrounded test results. The unrounded test results were preferably used for statistical evaluation. Also, some analytical details of the used test method, by means of a questionnaire, was included in the report form.

2.1 QUALITY SYSTEM

The Institute for Interlaboratory Studies in Spijkenisse, the Netherlands, has implemented a quality system based on ISO/IEC 17043:2010. 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 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 March 2017 (iis-protocol, version 3.4). 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

Nickel Release Determination

The samples were purchased from a local supplier and consisted of square metal pieces with a hole in one of the corners. The pieces were solid metal, prepared from one alloy and not plated or coated. The dimensions of each sample were approximately 2 x 2 x 0.2 cm and the hole had a diameter of approx. 5 mm. Samples were labelled #18575.
Twelve stratified randomly selected samples were tested using EN1811:2011 and single test results were averaged per three to check the homogeneity of the batch. The test results of the homogeneity tests, after exclusion of one clear outlying test result are shown in table 1.

	Nickel release (µg/cm^2/week) averaged per 3 items
sample #18575-1	0.597
sample #18575-2	0.592
sample #18575-3	0.605
sample #18575-4	0.593

Table 1: homogeneity test results of subsamples #18575

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

	Nickel release (µg/cm^2/week)
r (observed)	0.017
Reference method	Horwitz *)
0.3 x R (reference method)	0.087

Table 2: evaluation of the repeatability of subsamples #18575

*)The Horwitz formula is converted to µg/cm^2/week unit instead of a concentration

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

Surface Determination

A batch of metal leaves (piece of an earring) was obtained from a local supplier. From this batch, 150 plastic bags were filled each with one leaf. The samples were labelled #18576. No homogeneity tests were done because only surface determination has been requested for this sample. However, each leaf was weighed in advance to ensure no large differences in surfaces.

Three items of sample #18575 and one item of sample #18576 were sent to each of the participating laboratories on May 9, 2018.

2.5 ANALYSES

The participants were requested to determine Nickel release on sample #18575 and only the total surface on sample #18576, applying the analysis procedure that is routinely used in the laboratory. It was also requested to report some analytical details.

It was explicitly requested to treat the samples as if they were routine samples 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 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 reanalysis). Additional or corrected test results are used for data analysis and original test results are placed under 'Remarks' in the test 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 March 2017 (iis-protocol, version 3.4).
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 ISO 5725 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 them with a factor of 2.8.

3.2 GRAPHICS

In order to visualise 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, e.g. EN reproducibilities, the z-scores were calculated using a target standard deviation. This results in an evaluation independent of the variation of 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 targets 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.
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

During the execution of this proficiency test no problems were encountered. From the 114 participants, nine participants reported test results after the deadline for reporting and one other participant did not report any test results at all. In total 221 test results (Nickel release and surface determination) were received. Observed were 8 outlying test results, which is 3.6%. In proficiency studies outlier percentages of 3% - 7.5% are quite normal.

4.1 EVALUATION PER SAMPLE

In this section, the reported test results are discussed per sample. All statistical results reported on the sample are summarised in appendix 1. The abbreviations used in these tables are listed in appendix 6.

Test method EN1811:2011 does not have a true precision statement that mentions a repeatability and/or a reproducibility. In Annex A is mentioned that the measurement uncertainty in a 2008 interlaboratory study was 46%, while in Annex B is stated “The relative test method reproducibility in this ILC was 33.3%”. Both variations could not be met by far in previous iis PTs. Therefore, it was decided to use a target reproducibility derived from the Horwitz equation. This target is dependent on the measured Nickel concentration, surface and ranges from 54% at 0.3 μg Ni/cm^2/week up to 32% at 10 μg Ni/cm^2/week.

Sample #18575: Nickel release:

The determination of Nickel release at a low concentration level of 0.51 µg/cm^2/week was problematic. Four statistical outliers were observed. The calculated reproducibility after rejection of the statistical outliers is not in agreement with the target reproducibility estimated from the Horwitz equation. The low Nickel release level may (partly) explain the relatively large variation.

Sample #18576: Surface Determination:

The surface determination of the leaf may be problematic. Four statistical outliers were observed in the reported range of 0.2036 – 3.25 cm^2. No official test method exists for surface determination; therefore, no z-scores were calculated. However, the variation for this sample (13%) is large in comparison with the variation in previous PT's in which the surface determination was evaluated (4.9% - 6.7%) and also with the variation of the surface determination on a much simpler shaped sample #18575 (1.3%).

4.2 PERFORMANCE EVALUATION FOR THE GROUP OF LABORATORIES

A comparison has been made between the reproducibility as found for the group of participating laboratories and the target reproducibility estimated from the Horwitz equation in the next table:

Parameter	*unit*	*n*	*average*	*2.8 * sd*	*R (target)*
Nickel release	µg/cm^2/week	108	0.51	0.62	0.25
Contact surface	cm^2	99	9.55	0.35	n.a.

Table 3: reproducibilities of test results on sample #18575

From table 3 it can be concluded, without further statistical calculations, that the group of participating laboratories had problems with the analysis of Nickel release, when compared to the Horwitz target reproducibility.

Parameter	*unit*	*n*	*average*	*2.8 * sd*	*R (target)*
Surface Determination	cm^2	105	0.83	0.29	n.a.

Table 4: reproducibility of test results on sample #18576

4.3 COMPARISON OF THE PROFICIENCY TEST OF MAY 2018 WITH PREVIOUS PTS

	May 2018	*May 2017*	*May 2016*	*May 2015*
Number of reporting labs	113	122	125	123
Number of test results reported	221	122	124	119
Statistical outliers	8	14	8	11
Percentage outliers	3.6%	11%	6.5%	9.8%

Table 5: comparison with previous proficiency tests (Nickel Release determination only)

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

In table 6 the observed uncertainties in this PT are compared with the uncertainties as observed in the previous PTs.

	May 2018	*May 2017*	*May 2016*	*May 2015*	*May 2014*
Nickel Release	44%	26%	18%	28%	27-31%
Surface Determination	1.3 - 13%	1.3 - 6.7%	2.3 - 4.9%	1.7%	9 - 10%

Table 6: comparison of uncertainties (relative in %) of this PT and previous PTs

No quality improvement is visible in the Nickel Release determination, the uncertainty did increase compared to previous years.
The uncertainty of the surface determination of sample #18576 (leaf) is larger than the uncertainties of previous samples for surface determination and Nickel release samples (square plate) which was to be expected for the more difficult sample (leaf) that was used in the 2018 PT.

4.4 EVALUATION OF THE ANALYTICAL DETAILS

For sample #18575, some details of various analytical steps were requested, like the average volume of sweat simulant that was added to one piece of metal, the average surface of one piece of metal used for the calculation, the number of pieces of metal used for the Nickel release determination, which ratio in mL/cm² was used for the start solution versus the sample surface and whether the test vessel was pre-treated. For sample #18576, a description how the surface of the leaf was determined was requested. These reported details are summarized in appendices 2 - 4.
For sample #18575, in total 111 laboratories reported the average surface area used. The reported average surface area varied from 6.8 to 19.1 cm^2.
The majority of the participants reported a ratio of approx.1 ml/cm^2. The range of used ratios was 1.0 – 11.1 ml/cm^2. The range of initial volumes was 8.8 – 91.5 ml.
The majority of participants (75%) used 3 pieces for the Nickel release determination.
About 51% of the participants reported to have done a pre-treatment (with 5% (or higher) HNO_3 for at least 4 hours). Remarkably, 31% of the participants reported not to have done any pre-treatment and 21% did not answer this question (see appendix 3).
For sample #18576, only one question was requested: A brief description how the surface area was measured and calculated. Only 57% of the participants (65) reported a measurement and/or calculation method. A divers variety of methods was given (see appendix 4).

5 DISCUSSION OF REPORTED TEST METHOD DETAILS

<u>Determination of contact surface of the square test items #18575:</u>
In total 111 laboratories reported the average surface area used, see appendix 2. The reported average surface area for sample #18575 varied from 6.8 to 19.1 cm^2. After exclusion of twelve (12%!) statistically outlying data, the surface range narrowed from 9.15 to 10 cm^2.
The observed RSD of 1.3% is the same as in the previous PT.
In this PT, the overall $RSD_{Nickel\ release}$ for sample #18575 is 44%. This is the sum of the variation in contact surface determination and the variation in the Nickel determination. It can be

concluded that the variation in the surface determination of this (simple squared) object does not affect the overall variation of the Nickel release determination.

Volume of the start solution:
It was observed that a number of participants reported probably the end volume after dilution, e.g. 20 mL. The test method of EN1811:2011 prescribes that the amount of the start test solution to be used should be 1 ml per cm^2 surface area, which is in this PT about 10 ml per test item. Not all participants used this ratio.

Number of test items #18575 used for the Nickel release determination:
It was expected that the variation in this PT would have been smaller compared to previous PT's when all participants had tested all 3 test items as single measurement and reported an average. Regretfully, it is not clear if the participants reported an average value out of three single measurement or a total measurement divided by three. Neither is known if in a series of three test results a deviating test result was excluded.

Pre-treatment of vessel:
The vessel, used for leaving the sample in the sweat solution for a week, should be pre-treated with 5% Nitric acid for at least 4 hours, see paragraph 6.4 of EN1811:2011. This is necessary to remove any Nickel present from earlier use. When no pre-treatment is used, there will be a risk that the test result for Nickel release will be higher. To check whether some effect is visible, the test results of the laboratories that did not use any pre-treatment were compared with the test results after treatment with diluted nitric acid of at least 4 hours, see table 7.

	No pre-treatment	*≥ 5%HNO_3 pre-treatment for ≥4hrs*
Number of test results	32	51
Statistical outliers	2	2
Average	0.56 μg/cm^2/week	0.51 μg/cm^2/week
Standard deviation	0.232 μg/cm^2/week	0.193 μg/cm^2/week
RSD%	42%	38%

Table 7: influence of pre-treatment of test vessel

The effect of the acid pre-treatment of the vessel is visible, mainly in the variation. The variation in the test results from a vessel that was not pre-treated is higher than the variation in the test results from a correctly pre-treated test vessel. Quality improvement may be possible for this parameter. It is therefore strongly advised to follow the test method.

6 CONCLUSION

Although, it can be concluded that a large group of the participants have no problem with the determination on Nickel release, each participating laboratory needs 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.

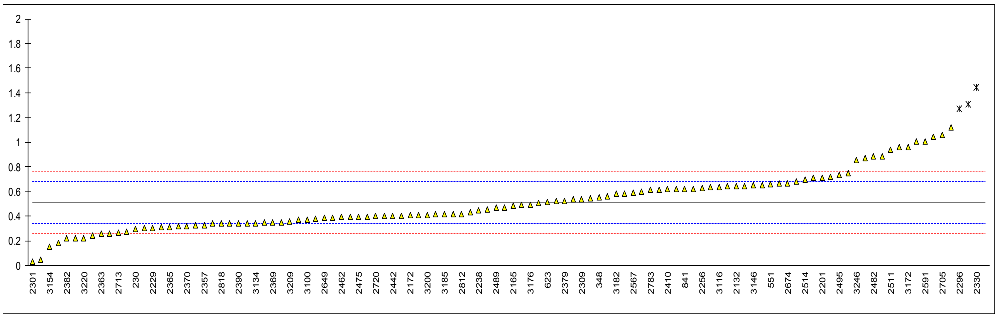
APPENDIX 1

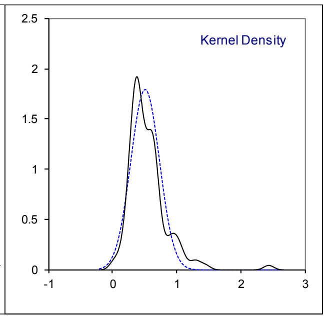
Determination of Nickel Release on sample #18575; result in μg/cm²/week

lab	method	value	mark	z(targ)	remarks
110	EN1811	0.8850		3.62	
213		-----		-----	
230	EN1811	0.2953	C	-2.06	Reported first as Volume instead of release
339	EN1811	1.0405		5.12	
348	EN1811 + AC	0.555		0.44	
362	EN1811	1.007		4.79	
551	EN1811	0.66		1.45	
623	EN1811	0.516		0.07	
840	EN1811	0.64		1.26	
841	EN1811	0.62		1.07	
2115	EN1811	0.75		2.32	
2121	EN1811	1.31	R(0.05)	7.71	
2129	EN1811 + AC	0.348		-1.55	
2132	EN1811	0.64		1.26	
2137	EN1811	0.962		4.36	
2165	EN1811 + AC	0.4860		-0.22	
2172	EN1811	0.411		-0.94	
2184	EN1811 + AC	0.633		1.19	
2190	EN1811	0.34		-1.63	
2201	EN1811	0.7149		1.98	
2213	EN1811	0.68		1.64	
2221	EN1811 + AC	0.04929		-4.43	
2229	EN1811 + AC	0.307		-1.95	
2238	EN1811 + AC	0.445		-0.62	
2241	EN1811	0.416		-0.90	
2247	EN1811	0.42		-0.86	
2255	EN1811 + AC	0.667		1.52	
2256	EN1811 + AC	0.632		1.18	
2266	EN1811 + AC	1.12		5.88	
2284	EN1811 + AC	0.399		-1.06	
2290	EN1811 + AC	0.646		1.32	
2293	EN1811	2.4347	R(0.01)	18.54	
2296	EN1811 + AC	1.2692	R(0.05)	7.32	Inhouse method based on EN1811 + AC
2297	EN1811 + AC	0.343		-1.60	
2301	EN1811	0.03		-4.61	
2309	EN1811 + AC	0.54		0.30	
2310	EN1811 + AC	0.60		0.87	
2311	EN1811 + AC	0.613		1.00	
2330	EN1811	1.4472	R(0.05)	9.03	
2347	EN1811 + AC	0.30		-2.01	
2350	EN1811	0.870		3.47	
2352	EN1811	0.3230		-1.79	
2357	EN1811	0.328		-1.74	
2363	EN1811 + AC	0.258		-2.42	
2365	EN1811	0.3139		-1.88	
2366	EN1811 + AC	0.397		-1.08	
2369	EN1811	0.35		-1.53	
2370	EN1811	0.322	C	-1.80	First reported 2.585
2375	EN1811 + AC	0.38		-1.24	
2377	EN1811	0.62		1.07	
2379	EN1811 + A1	0.523		0.13	
2380	EN1811 + AC	0.393		-1.12	
2382	EN1811	0.22		-2.78	
2385	EN1811	0.32		-1.82	
2390	EN1811	0.345		-1.58	
2410	EN1811	0.62		1.07	
2429	EN1811	0.412		-0.93	
2432	EN1811 + AC	0.370		-1.34	
2442	EN1811 + AC	0.403		-1.02	
2452	EN1811 + AC	0.5206		0.11	
2462	EN1811	0.391		-1.14	
2475	EN1811 + AC	0.394		-1.11	
2482	EN1811 + AC	0.8818		3.59	
2489	EN1811	0.47		-0.38	
2495	EN1811	0.7346		2.17	
2496	EN1811	0.47		-0.38	
2497	EN1811 + AC	0.311		-1.91	
2511	EN1811	0.940		4.15	
2514	EN1811	0.6964		1.80	
2532	EN1811	0.709		1.92	
2567	EN1811	0.59		0.78	
2573	EN1811 + AC	0.351		-1.52	
2590	EN1811	0.2438		-2.55	
2591	EN1811	1.0087		4.81	
2605	EN1811 + AC	0.432		-0.74	

lab	method	value	mark	z(targ)	remarks
2624	EN1811 + AC	0.18		-3.17	
2637	EN1811	0.26		-2.40	
2649	EN1811	0.39		-1.15	
2652	EN1811	0.4518		-0.55	
2653	EN1811	0.345		-1.58	
2674	EN1811	0.667		1.52	
2678	EN1811	0.220		-2.78	
2705	EN1811 + AC	1.063		5.33	
2713	EN1811	0.268		-2.32	
2720	EN1811	0.3982		-1.07	
2737	EN1811 + AC	0.4944		-0.14	
2783	EN1811	0.61		0.97	
2812	EN1811	0.42		-0.86	
2818	EN1811	0.342		-1.61	
2832	EN1811	0.51		0.01	
3100	EN1811 + AC	0.372		-1.32	
3110	EN1811	0.623		1.10	
3116	EN1811 + AC	0.634		1.20	
3118	EN1811	0.548		0.37	
3134	EN1811	0.345		-1.58	
3146	EN1811	0.65		1.36	
3150	EN1811 + AC	0.2733		-2.27	
3153	EN1811	0.5844		0.72	
3154	EN1811	0.152		-3.44	
3163		-----		-----	
3172	EN1811	0.963		4.37	
3176	EN1811	0.495		-0.14	
3182	EN1811	0.58		0.68	
3185	EN1811	0.418		-0.88	
3190	EN1811	0.403		-1.02	
3197	EN1811 + AC	0.72		2.03	
3200	EN1811	0.413		-0.93	
3209	EN1811	0.356		-1.47	
3210	EN1811	0.5615		0.50	
3220	EN1811	0.2204		-2.78	
3228	EN1811 + AC	0.65		1.36	
3237	EN1811	0.39		-1.15	
3246	EN1811	0.853		3.31	
3248	EN1811	0.537		0.27	

				Only with ratio <1.5	
	normality	OK		OK	
	n	108		89	
	outliers	4		4	
	mean (n)	0.509		0.497	
	st.dev. (n)	0.2228	RSD = 44%	0.1888	RSD = 39%
	R(calc.)	0.624		0.529	
	st.dev.(Horwitz)	0.0908		0.0890	
	R(Horwitz)	0.291		0.249	
Compare					
	R(EN1811:11)	0.170			



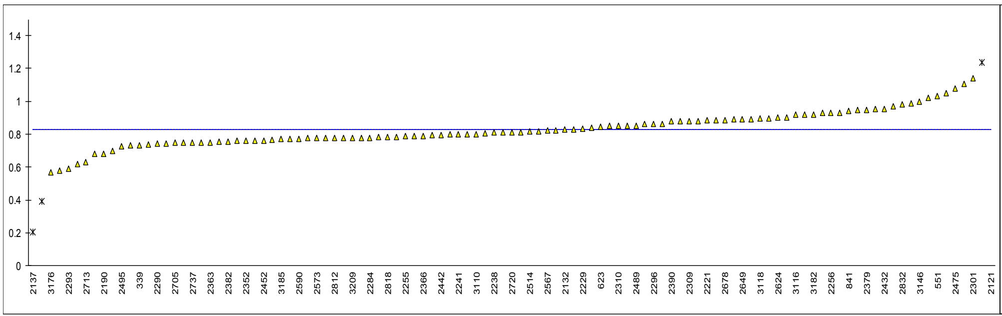
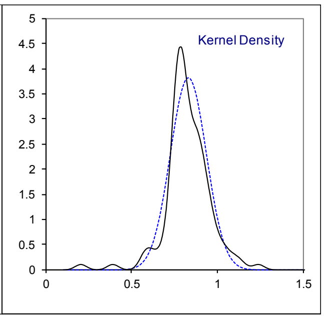


Determination of Surface determination on sample #18576; results in cm^2

lab	method	value	mark	z(targ)	remarks
110	See appendix 4	0.8796	C	-----	First reported 0.3028
213	See appendix 4	0.88		-----	
230	See appendix 4	0.9682		-----	
339	See appendix 4	0.73		-----	
348	See appendix 4	0.9534		-----	
362	See appendix 4	0.95	C	-----	First reported 0.48
551	See appendix 4	1.035022		-----	
623	See appendix 4	0.845		-----	
840		-----		-----	
841	See appendix 4	0.94		-----	
2115	See appendix 4	0.8		-----	
2121	See appendix 4	3.25	R(0.01)	-----	
2129	See appendix 4	1.105		-----	
2132	See appendix 4	0.83		-----	
2137	See appendix 4	0.2036	R(0.01)	-----	
2165	See appendix 4	0.764		-----	
2172	See appendix 4	0.758		-----	
2184	See appendix 4	1.0232		-----	
2190	See appendix 4	0.6825		-----	
2201	See appendix 4	0.821	C	-----	First reported 8.21
2213	See appendix 4	0.86		-----	
2221	See appendix 4	0.884		-----	
2229	See appendix 4	0.833		-----	
2238	See appendix 4	0.810		-----	
2241	See appendix 4	0.80		-----	
2247	See appendix 4	0.85		-----	
2255	See appendix 4	0.787		-----	
2256	See appendix 4	0.930		-----	
2266	See appendix 4	0.899		-----	
2284	See appendix 4	0.7802		-----	
2290	See appendix 4	0.742		-----	
2293	See appendix 4	0.5926		-----	
2296	See appendix 4	0.8618		-----	
2297	See appendix 4	0.745		-----	
2301	See appendix 4	1.139		-----	
2309	See appendix 4	0.88		-----	
2310	See appendix 4	0.85		-----	
2311	See appendix 4	0.864		-----	
2330	See appendix 4	0.8493		-----	
2347	See appendix 4	0.74		-----	
2350	See appendix 4	0.886		-----	
2352	See appendix 4	0.76		-----	
2357	See appendix 4	0.75		-----	
2363	See appendix 4	0.75		-----	
2365	See appendix 4	0.7482		-----	
2366	See appendix 4	0.790		-----	
2369	See appendix 4	0.73		-----	
2370	See appendix 4	0.9847		-----	
2375	See appendix 4	0.8		-----	
2377	See appendix 4	0.78		-----	
2379	See appendix 4	0.950		-----	
2380	See appendix 4	1.238	R(0.05)	-----	
2382	See appendix 4	0.754		-----	
2385	See appendix 4	0.8133		-----	
2390	See appendix 4	0.878		-----	
2410	See appendix 4	0.92		-----	
2429	See appendix 4	0.8115		-----	
2432	See appendix 4	0.954		-----	
2442	See appendix 4	0.793		-----	
2452	See appendix 4	0.76145		-----	
2462	See appendix 4	0.792		-----	
2475	See appendix 4	1.08		-----	
2482	See appendix 4	0.8043		-----	
2489	See appendix 4	0.853		-----	
2495	See appendix 4	0.7254		-----	
2496	See appendix 4	0.76		-----	
2497	See appendix 4	0.78978		-----	
2511		-----		-----	
2514	See appendix 4	0.8156		-----	
2532	See appendix 4	0.83		-----	
2567	See appendix 4	0.82		-----	
2573	See appendix 4	0.78		-----	
2590	See appendix 4	0.7740		-----	
2591	See appendix 4	0.781		-----	
2605	See appendix 4	0.928		-----	

lab	method	value	mark	z(targ)	remarks
2624	See appendix 4	0.90		-----	
2637		-----		-----	
2649	See appendix 4	0.89		-----	
2652	See appendix 4	0.7823		-----	
2653	See appendix 4	0.9	C	-----	First reported 1.8
2674	See appendix 4	0.78		-----	
2678	See appendix 4	0.887		-----	
2705	See appendix 4	0.7475		-----	
2713	See appendix 4	0.6318		-----	
2720	See appendix 4	0.812		-----	
2737	See appendix 4	0.7486		-----	
2783	See appendix 4	0.3899	C,R(0.05)	-----	First reported 3.899
2812	See appendix 4	0.78	C	-----	First reported 0.46
2818	See appendix 4	0.782		-----	
2832	See appendix 4	0.9840		-----	
3100	See appendix 4	0.84		-----	
3110	See appendix 4	0.8022		-----	
3116	See appendix 4	0.918		-----	
3118	See appendix 4	0.8943		-----	
3134	See appendix 4	0.7	C	-----	First reported 7.0
3146	See appendix 4	1.00		-----	
3150	See appendix 4	0.68		-----	
3153	See appendix 4	0.93		-----	
3154	See appendix 4	0.578		-----	
3163		-----		-----	
3172	See appendix 4	0.89		-----	
3176	See appendix 4	0.57		-----	
3182	See appendix 4	0.92		-----	
3185	See appendix 4	0.769		-----	
3190	See appendix 4	0.816		-----	
3197	See appendix 4	0.78		-----	
3200	See appendix 4	0.753		-----	
3209	See appendix 4	0.78		-----	
3210		-----		-----	
3220	See appendix 4	1.0467		-----	
3228	See appendix 4	0.77		-----	
3237	See appendix 4	0.78		-----	
3246	See appendix 4	0.62		-----	
3248	See appendix 4	0.889		-----	

normality	OK	
n	105	
outliers	4	
mean (n)	0.8301	
st.dev. (n)	0.10471	RSD = 13%
R(calc.)	0.2932	
st.dev.(target)	n.a.	
R(target)	n.a.	

APPENDIX 2

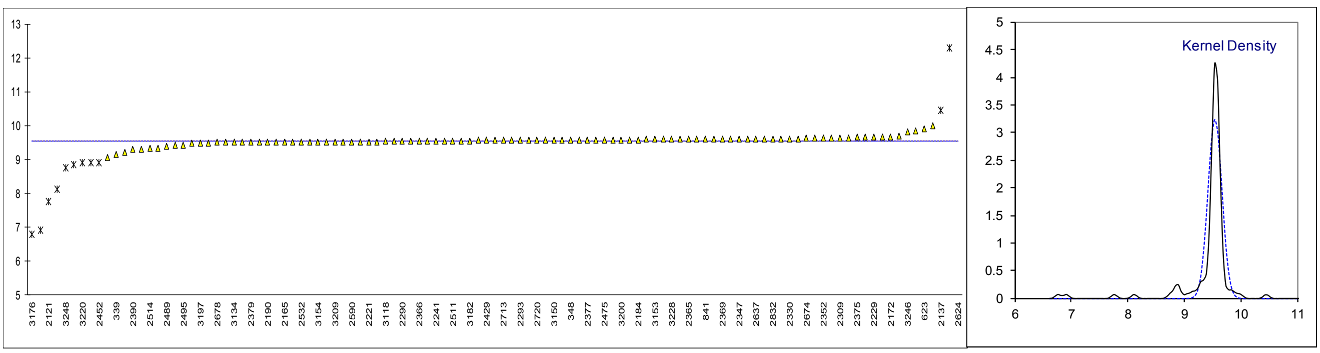
Average volumes added, average surfaces and number of pieces used of sample #18575

lab	average volume of sweat simulant added to one item (ml)		average surface of one item used (cm^2)		number of items used for Ni-release determination		Ratio in mL/cm² used for the start solution versus the sample surface
110	10.00		9.506		3		1:1
213	-----		-----		-----		
230	10		9.589		3		
339	91.5		9.15		-----		1:10
348	15		9.571		3		1.6
362	9.5		9.41		1		
551	12		9.828		3		1.22
623	9.9		9.9		2		1:1
840	10		9.53		2		1:1
841	10.0		9.6		-----		
2115	12		9.2		-----		
2121	20		7.77	R(0.01)	2		2.5
2129	9.52		9.52		3		1:1
2132	12.5		12.3	R(0.01)	2		~1:1
2137	12		10.46	R(0.01)	3		1.1467
2165	10.0		9.52		3		Approximately 1:1
2172	10		9.670		1	Per trail	1/1
2184	10		9.584		3		1:1
2190	9.5	C, fr 20	9.52		3		
2201	9.60		9.60		3		1:1
2213	10		9.69		3		
2221	12		9.5215		1		1.26
2229	9.66		9.66		3		1:1
2238	9.5		9.5		3		1
2241	10.50		9.545		3		1.1
2247	12	C, fr 25	9.49		3		1:1
2255	10		9.303		3		1:1
2256	10		9.637		3		around 1:1 (9.637:10)
2266	20		10		2		1
2284	10.0		9.5981		3		10:9.6 = 1.04
2290	9.53		9.53		3		
2293	25		9.57		3		1:1
2296	11		9.564		3		1:1
2297	10		9.55		3		1:1
2301	10		9.66		3		
2309	10		9.64		3		1:1
2310	10		8.9	R(0.01)	3		1ml/cm²
2311	10		9.52		3		1:1
2330	10		9.6041		1		1:1
2347	9.60		9.60		3		1:1
2350	10	C, fr 25	9.584		3		1:1 (= 10 mL used)
2352	9.65		9.63		3		
2357	10		9.57		3		
2363	9.6		9.58		3		1:1
2365	10	C, fr 13	9.60		3		13ml / 9.6cm2 = 1.3542
2366	10.0		9.54		-----		1:1
2369	9.6		9.6		3		1:1
2370	10		9.6		3		10 ml / 9.6 cm2
2375	9.65		9.65		3		
2377	10		9.58		3		10 ml / 9.6 cm2
2379	20		9.51		1		9.50 ml/9.51 cm2
2380	-----		-----		-----		1:1
2382	9.580		9.578		3		1:1
2385	12		9.6		1		
2390	9.3		9.3		3		1:1
2410	12		9.6		3		1:1
2429	9.6		9.5612		1		1:1
2432	17		9.530		3		
2442	10.00		9.557		3		1:1
2452	8.9	C, fr 20	8.9	R(0.01)	3		
2462	9.50		9.52		3		1:1
2475	9.58		9.58		1		1
2482	15		9.61		3		
2489	10		9.4		3	1 per trial	10
2495	50		9.4206		3		5.3
2496	10		9.54		3		10
2497	15		9.05076		3		1.5
2511	9.55		9.55		3		
2514	10.0		9.32		3		1:1
2532	25		9.52		3		25 ml versus 10-25cm2
2567	10		9.33		3		1:1
2573	10		9.55		3		1:1
2590	10		9.5208		3		1.05

lab	average volume of sweat simulant added to one item (ml)		average surface of one item used (cm²)		number of items used for Ni-release determination		Ratio in mL/cm² used for the start solution versus the sample surface
2591	15		9.59		3	1 per trial	1:1
2605	9.48		9.48		3		1:1
2624	20		19.11	R(0.01)	3		1:1
2637	10		9.6		-----		
2649	10	C, fr 20	9.6		-----		
2652	10		9.57		3		
2653	10		6.92	R(0.01)	3		
2674	10	C, 15	9.62		3		1.5:1
2678	10		9.496		3		
2705	50.0	Final volume	9.521		3		1
2713	15	C, fr 20	9.569		2		-
2720	9.6		9.57		1		1:1
2737	10		9.5215		3		1:1
2783	90		8.1239	C,R(0.01)	2		1.11
2812	20	C, fr 25	8.84	R(0.01)	3		2,26 mL/cm2
2818	9.579		9.58	C	3		
2832	11	Final vol. 75ml	9.6		3		1,1 ml/cm2 circa
3100	9.57		9.57		1		1:1
3110	10		9.52		3		
3116	10		9.66		3		1
3118	12		9.525		-----		1.26 mL/cm2
3134	10.0		9.5		3		1:1
3146	9.6		9.6		3		1:1
3150	10		9.57		3		
3153	9.6		9.589		3		1:1
3154	50		9.52		3		
3163	-----		-----		-----		
3172	9.64		9.64		3		
3176	14		6.775	R(0.01)	3		2,06
3182	10.0		9.55		3		1:1
3185	9.6		9.57		3		1:1
3190	9.52		9.52		3		1:1
3197	9.48		9.48		3		1:1
3200	9.60		9.58		3		1:1
3209	9.5		9.52		3		1:1
3210	10		9.52		2		
3220	10		8.8935	R(0.01)	2		1;1
3228	9.59		9.59		3		1
3237	15		9.62		3		1,56
3246	10		9.8		3		1.02
3248	8.76		8.76	R(0.01)	3		1:1

normality	not OK	
n	99	
outliers	12	
mean (n)	9.553	
st.dev. (n)	0.1236	RSD = 1.3%
R(calc.)	0.346	
st.dev.(target)	n.a.	
R(target)	n.a.	

Lab 2783,: first reported 81.329
Lab 2818: first reported 25



APPENDIX 3

Reported analytical details for sample #18575

lab	test vessel pre-treated	hours the test vessel cleaned	Solution cleaning test vessel
110	No		
213	--		
230	--		
339	Yes	15 hrs	HNO3 5%
348	No		
362	--		
551	Yes	4 hrs	HNO3 20%
623	Yes	4 hrs	Nitric Acid
840	Yes	24 hrs	5% Nitric acid solution
841	--		
2115	No		
2121	No		
2129	No		
2132	No		
2137	Yes	5 hrs	5%HNO3
2165	No	--	--
2172	Yes	4 hrs	4M nitric acid
2184	No	--	--
2190	--		
2201	Yes	4 hrs	dilute nitric acid
2213	Yes		yes
2221	Yes	6 mins	Sodium dodecyl sulphate
2229	Yes	4 hrs	dilute nitric acid
2238	Yes	24 hrs	5%HNO3
2241	Yes	12 hrs	10% HNO3
2247	No	-	-
2255	Yes	4 hrs	5% HNO3
2256	Yes	4 hrs	Diluted nitric acid
2266	No		
2284	Yes	24 hrs	5% HNO3
2290	--		
2293	Yes	4 hrs	Nitric acid at 1%
2296	No		
2297	Yes	24 hrs	HNO3
2301	--		
2309	No		
2310	Yes	4 hrs	Dilute HNO3 and deionized water
2311	Yes	4 hrs	5% Nitric acid and deionized water
2330	Yes	12 hrs	20% Nitric acid
2347	Yes	15 mins	Grade 1 water
2350	No		
2352	No		
2357	--		
2363	Yes	4 hrs	5% HNO3
2365	Yes	4 hrs	5% HNO3
2366	Yes	4 + 0.5 hrs	nitric acid solution and DI water
2369	Yes	4 hrs	1:1 HNO3:H2O
2370	Yes	20 mins	70% Concentrated nitric acid.
2375	--		
2377	Yes	4 hrs	Dilute Nitric Acid
2379	Yes	2 hrs	5% HNO3
2380	Yes	8 hrs	5% Nitric acid solution
2382	Yes	4 hrs	5%HNO3
2385	No		
2390	No		
2410	Yes	12 hrs	5 % HNO3
2429	Yes	4 hrs	5% HNO3
2432	--		
2442	Yes	12 hrs	5% HNO3
2452	No		
2462	Yes	8 hrs	5% nitric acid
2475	Yes	5 hrs	HNO3 5%
2482	No		
2489	No	-	-
2495	No		
2496	Yes	24 hrs	20% HN03
2497	No		
2511	--		
2514	Yes	4 hrs	5.0% Nitrc Acid
2532	Yes	4 hrs	Yes, 5% Nitric Acid
2567	No		
2573	Yes	5 hrs	5% HNO3
2590	No		
2591	No		

lab	test vessel pre-treated	hours the test vessel cleaned	Solution cleaning test vessel
2605	Yes	4 hrs	5% HNO3
2624	Yes	12 hrs	HNO3 5%
2637	--		
2649	No		
2652	--		
2653	--		
2674	Yes	4 hrs	5%HNO3
2678	--		
2705	Yes	8 hrs	HNO3 diluted
2713	No	-	-
2720	Yes	4 hrs	5%HNO3
2737	Yes	4 hrs	5% Nitric acid
2783	No		
2812	No		
2818	--		
2832	Yes	4 hrs	HNO3 5%
3100	Yes	4 hrs	5%(m/m) Dilute nitric acid
3110	--		
3116	Yes	4 hrs	Nitric acid bath
3118	No		
3134	Yes	24 hrs	5 % nitric acid
3146	No		
3150	No		
3153	Yes	4 hrs	5% HNO3
3154	--		
3163	--		
3172	--		
3176	Yes	4 hrs	Nitric asid
3182	Yes	24 hrs	10% Nitric acid
3185	No	--	--
3190	Yes	24 hrs	washing agent,then deionized water.
3197	Yes	4 hrs	5% HNO3
3200	Yes	24 hrs	5% HNO3
3209	Yes	4 hrs	D.I. Water
3210	--		
3220	Yes	3-4 hrs.	Approx. 5%Nitric acid
3228	Yes	>12 hrs	20% HNO3
3237	No		
3246	No		
3248	Yes	24 hrs	Artificial Sweat Solution

APPENDIX 4

Reported Surface Determination details for sample #18576

lab	The surface of the leaf measured and calculated?
110	Object was first treated as 3 separate shapes: 2 Triangles & 1 Rectangle.
213	
230	By using grid paper
339	
348	Measurements with caliber and enlarged photo over graph paper. Regular geometric figures were used t
362	
551	
623	
840	
841	
2115	
2121	we made an enlargment of the sample on a sheet of paper to determine the leaf area by mass surface.
2129	
2132	Vernier Calliper
2137	
2165	Project the sample onto the 1 mm2 grid paper, then count the number of cells.
2172	assume sample is ellipse, calculate its surface area then subtract the surface area of hollow parts
2184	Measure the surface with digital calliper.
2190	
2201	Suppose the leaf is composed of tw0 triangles and calculate all surface area including thickness.
2213	
2221	Sample area = plane area * 2 + lateral area. 1. Plane area: Magnify the projection onto a paper with
2229	
2238	Vernier callipers, measuring simulated graphics area.
2241	The up/down area is calculated by weight/density/thickness. The side area is done by digital slider.
2247	sample shape was fitted under different mathematical shapes & area calculation done accordingly.
2255	The object considered as Ellipse & outside circle. Eliminate area of triangular blank portion
2256	Draw the shape of the sample on standard grid paper and count the grid cells (1 sq. mm per cell)
2266	Microscope
2284	Drawing the outline on grid paper, then calculate the area by the ratio of weight to area.
2290	
2293	We use millimetre paper and put on it the sample, then we increase the image.
2296	
2297	The method of counting the amount of checks is used for the surface area of irregular metal leaf
2301	
2309	By using Vernier Calliper scale & Area calculation formula
2310	we calculate the surface area of object (ellipse and circle) using Vernier Calliper
2311	
2330	6(1/2xwxh)+8(wxl)-4πr2+2 ðrh+5(wxh)-10(π/4xDxd)-12(1/2xwxh)
2347	
2350	We calculated the square area by subtracting the area of the rim and the holes in the centre.
2352	
2357	
2363	
2365	
2366	According to M=ρV, 1. get weight (M). 2.getmain component with XRF, 3caluclated “V, than measured thickness, so sample area can be measured
2369	
2370	Total surface area = surface area of leave (both sides) + surface area of hollow circle at the bottom (both sides) + surface area on both sides of leaf + surface area on both sides of the hollow circle at the bottom + 15 surface area on both sides of the hollow leaves – 15 leaf hollow surface area.
2375	
2377	use calibrated calliper to calculate the object surface
2379	
2380	First think it as a rectangle shape with small whole like circular. Then we deduct four triangle which is around four blank place
2382	Treat the leaf as the total of two triangle. Then minus the hollow area for the surface area.
2385	The sample was divided into smaller areas and measured separately as a rectangle and summarized
2390	Using Ellipse, Circle & Rectangle Formula
2410	
2429	The area of the sample is regarded as a regular and easily calculated area by filling.
2432	
2442	We used graph to calculate the separate area of each part and then finally added all the area.

lab	The surface of the leaf measured and calculated?
2452	
2462	Vernier Calliper
2475	
2482	Sample form copied to paper using magnification, empty spaces cut out. Weighing against paper
2489	Measured with Vernier calibre, Length, width and thickness and calculated. Holes portions substract
2495	by comparison with a reference sample by software ImageJ
2496	Draw with Vernier callipers number lattice.
2497	3D-scanner
2511	
2514	We consider it as like as Ellipse and every hole consider as Triangle
2532	
2567	Considered the sample as Ellipse and used formula A= 2Pi x a x b; then deduct area of hole.
2573	We put the metal leaf sample onto a graph paper and took a picture. Then zoom in the photo so that we can count the amount of checks of the graph paper. For the checks more than half of which are covered by the leaf, we count them into the area. For the checks with less than half covered by the leaf, we just waive them. This counting should be performed by more than 3 person. Finally, we calculate the average as the final area result..
2590	I used the following geometrical figures: rectangle, circumference, cylinder and trapezium
2591	With the programme Image J
2605	Use the area measure machine to calculate the sample area.
2624	
2637	
2649	Used a graph paper, calculated the percentage of each box and edge length, slid callipers for thick.
2652	
2653	tracing the item on the graph paper and then count the number of squares covered by the item
2674	
2678	
2705	ISO 1811: consider geometrical forms: Rhombus (1/2*0.65*1.15*2)
2713	-
2720	By division area filling and calculated
2737	
2783	Used ImageJ software and digital callipers.
2812	The top is circle. It is thought like the middle circle. The bottom of the object is triangle
2818	
2832	we have zoom in a photo (23 magnification), then cut out perimeter, take the weight of the paper
3100	Approximately the area of the ellipse, minus the area of the hole.
3110	
3116	Use common geometrical shapes to calculate the surface area
3118	measured use digital calliper
3134	Scanning. magnifying, cutting, weighting and comparing its mass with mass of sheet of known area.
3146	We have determined the area using an ellipse
3150	
3153	Geometric approximation
3154	
3163	
3172	3D Scanner
3176	
3182	Drawing on graph paper and calculate the area.
3185	Calculated by hand using digital calliper measured the length.
3190	Calculated the area of sample as an integral whole ellipse. Then minus the area carved part.
3197	
3200	
3209	
3210	
3220	Based on graphical method
3228	Using area measure machine
3237	
3246	
3248	by making the contour of the sample on the graph paper

APPENDIX 5

Number of participants per country

5 labs in BANGLADESH
1 lab in BRAZIL
1 lab in BULGARIA
2 labs in CAMBODIA
6 labs in FRANCE
7 labs in GERMANY
1 lab in GREECE
1 lab in GUATEMALA
7 labs in HONG KONG
8 labs in INDIA
3 labs in INDONESIA
7 labs in ITALY
3 labs in KOREA
1 lab in LUXEMBOURG
1 lab in MAURITIUS
1 lab in MOROCCO
1 lab in NETHERLANDS
35 labs in P.R. of CHINA
1 lab in PAKISTAN
2 labs in SPAIN
1 lab in TAIWAN R.O.C.
2 labs in THAILAND
3 labs in TUNISIA
6 labs in TURKEY
2 labs in U.S.A.
2 labs in UNITED KINGDOM
4 labs in VIETNAM

APPENDIX 6

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	= probably an error in calculations
U	= test result probably reported in a different unit
W	= test result withdrawn on request of participant
ex	= test result excluded from the statistical evaluation
n.a.	= not applicable
n.e.	= not evaluated
n.d.	= not detected
fr.	= first reported

Literature:

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