

Report

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Weighing Proficiency Testing Scheme for the STA, Round 1 Final Report

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Final Report

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ABSTRACT

This report presents the results of the first round of the particulate weighing proficiency testing scheme operated by NPL for the Source Testing Association completed in November 2007.

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Approved on behalf of the Managing Director, NPL
by Martyn Sene, Director, *Quality of Life Division*

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Weighing Proficiency Testing Scheme For The STA, Round 1

by

Matthew Williams, Rod Robinson

1. INTRODUCTION

This report describes the results of the first round of a weighing measurement proficiency-testing scheme carried out by the National Physical Laboratory for the STA.

The weighing proficiency testing (PT) scheme provides a way of assessing the performance of laboratories by a series of regular inter-laboratory comparisons. The test samples consisted of foil shims, with known masses provided by traceable measurements carried out by NPL, and solutions containing known mass of dissolved salt, simulating a probe washing solution. The results of each participant's analyses were compared to the assigned values. The set of results have been reported anonymously, and in addition each participant has been made aware of their own results. In this way participants are able to assess their performance in relation to other laboratories.

2. PT SCHEME DESCRIPTION

Thirty-two STA member companies took part in the first round of the scheme, which involved the round robin measurement of shims and simulated probe washing solutions.

The PT scheme assesses the measurement by the participants, of the masses of metal foil shims, and the masses of the residual salt following evaporation of the solutions. The test samples each have a known, assigned value, determined by NPL. In this PT scheme each participant received a separate test sample.

The shims were individually weighed by NPL, after being cleaned using alcohol and then heated in an oven in accordance with the procedure in BS EN 13284-1.

The washing solution samples were decanted by pipette from a bulk stock solution. The bulk solution contained a known mass of salt (NaCl) in a measured volume of purified water. The solutions delivered to the participants each contained a nominal mass of salt of 5 mg. The shims had nominal masses in the range 114 mg to 177 mg.

The participants were not told the masses of the shims or the salt content of the solution. Each participant was required to weigh their shim using a weighing procedure in accordance with BS EN13284-1. The shims were dried in a drying oven for at least one hour, at a minimum of 180 °C, and then cooled down to ambient temperature in a desiccator located in the weighing room for at least 4 hours. The shims were then weighed and the weight recorded after 1, 2 and 3 minutes and the result extrapolated to zero time and reported.

The washing solution was split by the participants into three equal parts. These were then evaporated in following their standard methodology and weighed, again in accordance with BS EN 13284-1. The results of the three washing solution weighings were reported. The sum

of these three weights should equal the 5mg known to be in the solutions provided to the participants.

The results of these analyses were returned to the STA and NPL.

The results of each analysis were expressed as percentage differences from the true value. This allows a comparison to be made between participants with different shim weights. The results are presented in graphical form in Figure 1, and a summary of the results is also given in Table 2. The participants are listed in random order.

There are a number of ways in which the results of PT schemes can be interpreted. The most straightforward technique is to examine the percentage differences of the reported results from the true value, as has been applied above to this PT scheme. It is then left to the participants to gauge how well they have performed.

A more refined interpretation of PT scheme results involves the calculation of a performance score for each result. This is usually based on comparing the results achieved against an assigned target standard deviation, σ . The simplest form of this is the 'z score'. This is calculated by dividing the deviation of each result from the true value by σ , see Equation 1.

$$z = \frac{x - T}{\sigma} \quad \text{Equation 1}$$

where:	z	z score
	x	value obtained by participant
	T	true value for test sample
	σ	assigned value for standard deviation

This provides a z score for each result, which can be compared with other z scores either by other participants or by the same participant on different rounds of the scheme. If a suitable value of σ is chosen then the z score also provides a method of deciding decision limits for the PT scheme. In general, if all results are normally distributed about the true value of the test sample and a reasonable value of σ has been chosen, then few (< 5 %) of the z scores should lie outside ± 2 . z scores lying outside ± 3 would be strongly indicative of a true bias in the reported value, rather than random uncertainty. From this it is possible to apply a classification as follows:

$ z \leq 2$	satisfactory
$2 > z < 3$	questionable
$ z \geq 3$	unsatisfactory

These limits allow each participant to judge their own performance and can be used to indicate potential problems. The target standard deviation is usually taken to be a value, which is fit for purpose for the measurements being made. The value of σ used for this scheme has been selected as 0.1 mg, this has been chosen to be 10% of a 1 mg particulate loading, and is also close to the 0.11 mg standard deviation observed in the results.

A small 0.07 mg bias was observed in the average of the reported results, and this has been corrected for. It is assumed this was caused by further loss of volatile material from the shims when placed in the oven by participants.

Participants who attain z scores of 2 or higher should investigate the cause of the performance with an aim to improving their performance in subsequent rounds. Those with z scores of 3 or higher should put in place a documented mechanism to correct any issues identified as soon as possible.

3. RESULTS

The results for the shim weighings are presented in Table 1.

Company I/D	Shim ID	Initial Shim Weight (mg)	Assigned shim weight	Reported Shim Weight (mg)	Deviation of Shim Weight (mg)
1	8	145.24	145.165	145.2	0.03
2	28	142.51	142.435	142.4	-0.04
3	1	132.88	132.805	132.7	-0.11
4	32	126.63	126.555	126.59	0.03
5	14	141.65	141.575	141.58	0.00
6	22	113.96	113.885	113.9	0.01
7	10	139.08	139.005	139.01	0.00
8	11	120.92	120.845	120.47	-0.38
9	29	127.31	127.235	127.2	-0.04
10	23	164.89	164.815	165	0.18
11	2	151.95	151.875	151.98	0.10
12	6	152.84	152.765	152.77	0.00
13	13	133.61	133.535	133.51	-0.03
14	4	150.84	150.765	150.82	0.05
15	15	136.56	136.485	136.48	-0.01
16	30	134.05	133.975	133.94	-0.04

17	31	124.77	124.695	124.68	-0.02
18	3	152.74	152.665	152.8	0.13
19	17	150.2	150.125	150.11	-0.02
20	19	139.1	139.025	138.9	-0.13
21	5	140.96	140.885	140.903	0.02
22	27	141.18	141.105	141.08	-0.03
23	20	148.42	148.345	148.3	-0.05
24	24	125.11	125.035	125.18	0.14
25	21	141.73	141.655	141.7	0.04
26	7	147.46	147.385	147.6	0.21
27	18	133.25	133.175	133	-0.18
28	26	176.54	176.465	176.5	0.03
29	16	138.61	138.535	138.48	-0.06
30	12	155.91	155.835	155.82	-0.02
31	9	144.62	144.545	144.6	0.05

Table 1. Difference, in mg, between reported results and NPL assigned value

As can be seen, the agreement with the assigned absolute shim weights is generally good. However, a comparison has to be made with the typical masses of particulate measured on filters, which is of the order of 1- 10 mg. The standard deviation of the differences is 0.11 mg. This provides an indication of the variability of weighing across the participants.

The z score results for the shim measurements are given in Table 2.

Participant ID	Shim ID	Percentage deviation	Z Score $\sigma = 0.1$
1	8	0.02	0.35
2	28	-0.02	0.35
3	1	-0.08	1.05
4	32	0.03	0.35
5	14	0.00	0.05
6	22	0.01	0.15
7	10	0.00	0.05
8	11	-0.31	3.75
9	29	-0.03	0.35
10	23	0.11	1.85
11	2	0.07	1.05
12	6	0.00	0.05
13	13	-0.02	0.25
14	4	0.04	0.55
15	15	0.00	0.05
16	30	-0.03	0.35
17	31	-0.01	0.15
18	3	0.09	1.35
19	17	-0.01	0.15
20	19	-0.09	1.25

21	5	0.01	0.18
22	27	-0.02	0.25
23	20	-0.03	0.45
24	24	0.12	1.45
25	21	0.03	0.45
26	7	0.15	2.15
27	18	-0.13	1.75
28	26	0.02	0.35
29	16	-0.04	0.55
30	12	-0.01	0.15
31	9	0.04	0.55

Table 2. Shim results, Percentage difference and z scores

The z score results for the shims are generally good, with only two participants with z-scores greater than 2. Figures 1 and 2 show these results graphically.

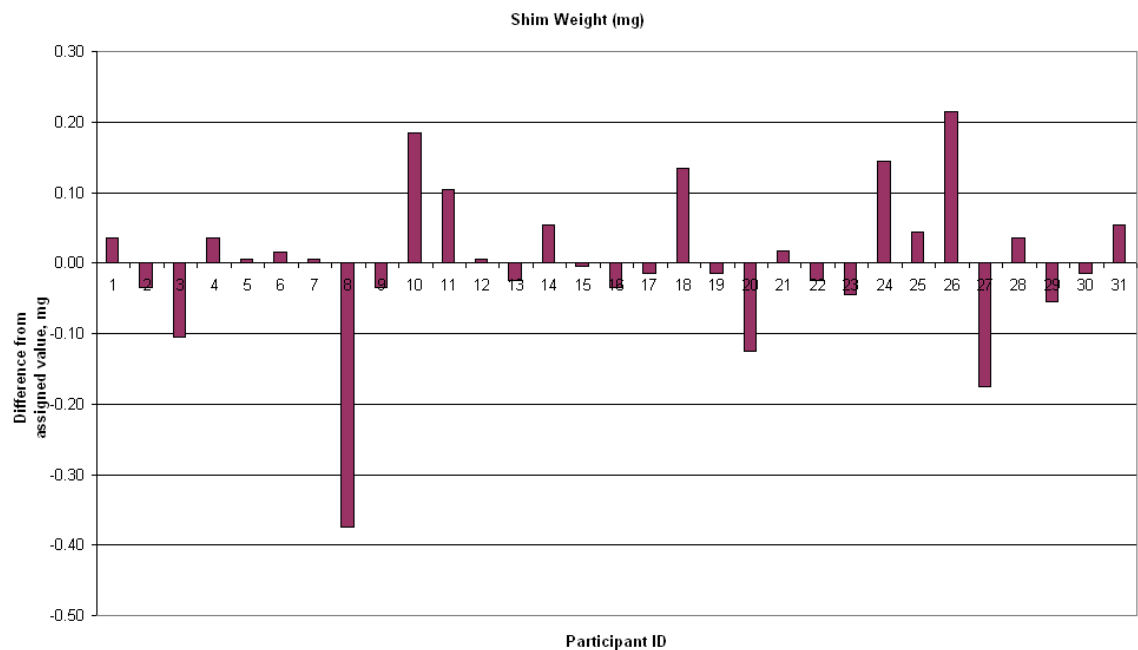


Figure 1, Difference in shim weights from assigned values.

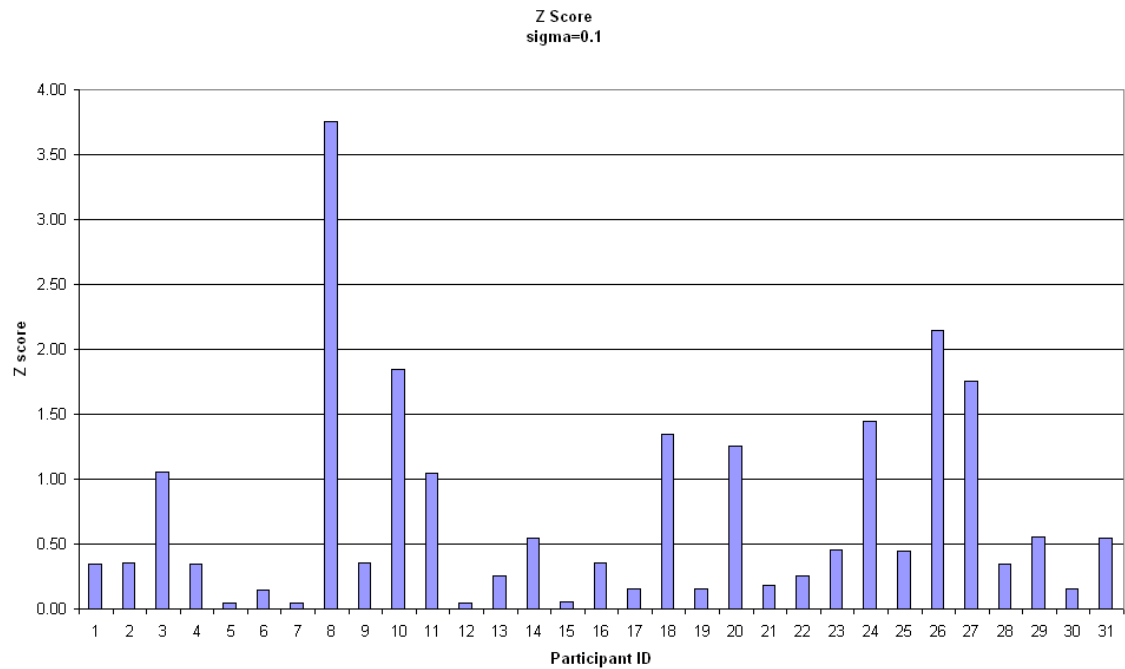


Figure 2, Z scores for shim weighing results.

The results for the solution evaporation and weighing are given in Table 3. This gives the results from weighing the residuals from the 3 portions of the solution and the total mass of residue from all three, which should be equal to the 5 mg salt present in the provided samples.

Participant ID	Mass Salt Assigned value (mg)	Wash one (mg)	Wash two (mg)	Wash Three (mg)	Total Wash Weights (mg)	Deviation from assigned value (mg)
1	5	2.6	2.4	2.5	7.5	2.50
2	5	0.8	0.5	0.5	1.8	-3.20
3	5	1.9	1.8	2	5.7	0.70
4	5	2.2	1.8	2	6	1.00
5	5	1.68	1.6	1.63	4.91	-0.09
6	5	1.7	1.9	1.6	5.2	0.20
7	5	2.67	2.23	2.12	7.02	2.02
8	5	2.2	2.17	2.03	6.4	1.40
9	5	5.4	4.9	0	10.3	5.30
10	5	1.7	1.7	1.7	5.1	0.10
11	5	1.69	1.59	2.14	5.42	0.42
12	5	0.8	0.5	0.6	1.9	-3.10
13	5	2.003	1.9	1.923	5.826	0.83
14	5	2.01	2	1.84	5.85	0.85
15	5	1.75	1.74	1.97	5.46	0.46
16	5	1.4	1.26	1.54	4.2	-0.80
17	5	0.17	0.46	1.17	1.8	-3.20
18	5	1.7	1.9	1.8	5.4	0.40

19	5	1.5	1.5	1.5	4.5	-0.50
20	5	1.7	2.1	2	5.8	0.80
21	5	1.556	1.835	2.522	5.913	0.91
22	5	1.6	1.1	2	4.7	-0.30
23	5	2.9	1.3	2.2	6.4	1.40
24	5	2.5	2.6	3.8	8.9	3.90
25	5	1.62	1.81	1.89	5.32	0.32
26	5	1.8	2.1	1.9	5.8	0.80
27	5	1.5	1.9	1.3	4.7	-0.30
28	5	1.5	4.3	2.8	8.6	3.60
29	5	1.7	1.7	1.7	5.1	0.10
30	5	1.4	1.38	1.24	4.02	-0.98
31	5	1.41	1.19	1.2	3.8	-1.20

Table 3. Difference, in mg, between reported results and NPL assigned value

Table 4 presents the washing solution results as percentage difference from the assigned value and as a z-score, with a target standard deviation of 1mg.

Participant ID	Percentage Difference	Z Score $\sigma = 1 \text{ mg}$
1	50.00	2.50
2	-64.00	3.20
3	14.00	0.70
4	20.00	1.00
5	-1.80	0.09
6	4.00	0.20
7	40.40	2.02
8	28.00	1.40
9	106.00	5.30
10	2.00	0.10
11	8.40	0.42
12	-62.00	3.10
13	16.52	0.83
14	17.00	0.85
15	9.20	0.46
16	-16.00	0.80
17	-64.00	3.20
18	8.00	0.40
19	-10.00	0.50
20	16.00	0.80
21	18.26	0.91

22	-6.00	0.30
23	28.00	1.40
24	78.00	3.90
25	6.40	0.32
26	16.00	0.80
27	-6.00	0.30
28	72.00	3.60
29	2.00	0.10
30	-19.60	0.98
31	-24.00	1.20

Table 4. Washing solutions, Percentage differences and z scores

Figures 3 and 4 present the percentage difference and z-scores for the washing solution results.

The z-score for the solution evaporation and weighing results has been calculated using a target standard deviation, σ , of 1 mg. This relatively lenient target standard deviation has been chosen because of the additional complexity of required to measure a washing solution. Despite this relatively lax target (equivalent to 20% of the assigned value of 5 mg), the results are very variable, with 5 participants gaining z-scores in excess of 3. It is also interesting to note that in many of these cases there is significant variability between the weights of the three split washings, indicating possible sources of variation due to contamination or material loss during sample handling.

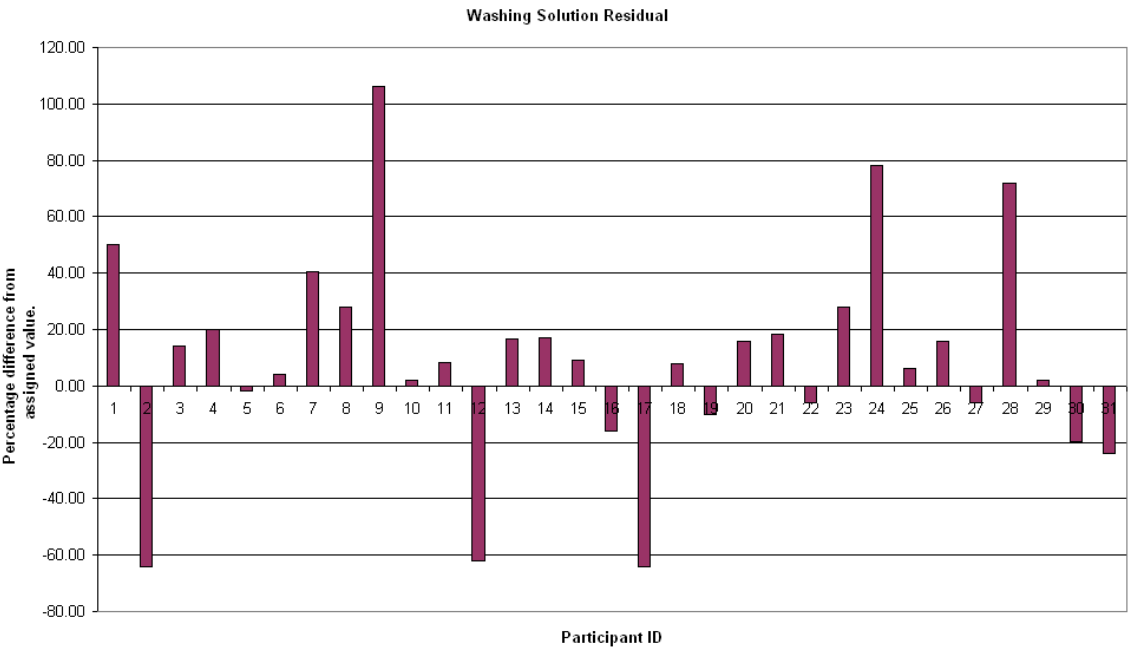


Figure 3. Percentage Difference in washing solution residual weight from assigned values.

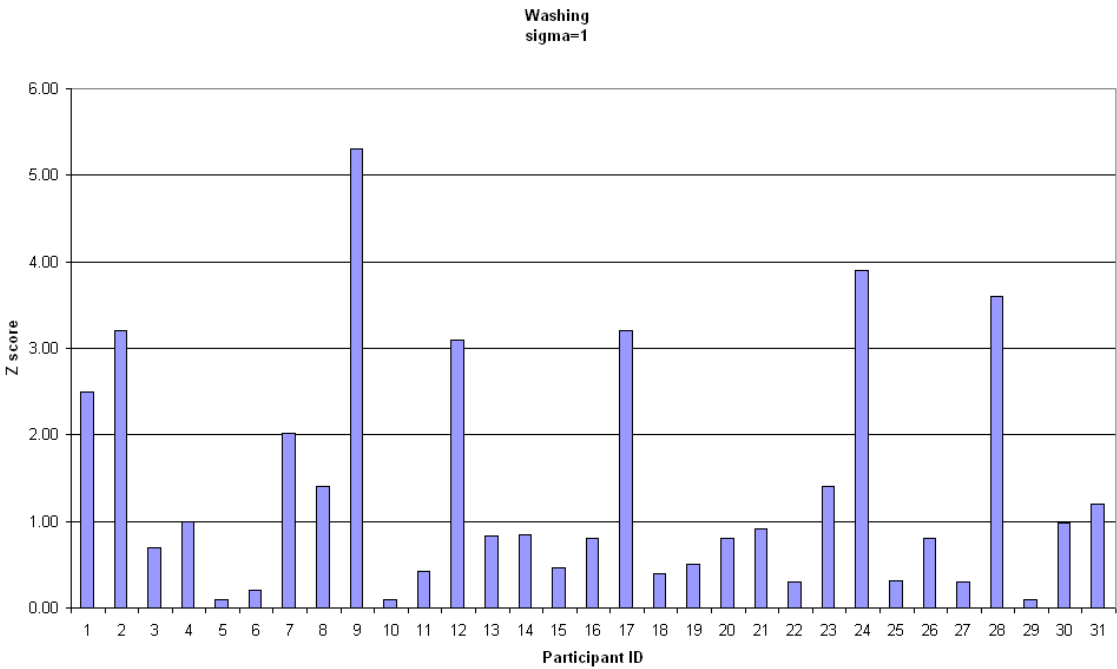


Figure 4. Washing Solution residue, z Score

4. CONCLUSIONS

The results from the shim measurements are generally encouraging and indicate that most organisations have their balances under calibration.

The results from the solution evaporation and weighing are more concerning and show some significant uncertainties are present in this procedure. Further investigation into the causes of the performance seen for washing solution weighing is recommended.

5. ACKNOWLEDGEMENTS.

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