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Particulate Proficiency Testing Scheme, Round 3
Final Report

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ABSTRACT

This report presents the results of the third round of the particulate particulate proficiency testing scheme operated by NPL completed in September 2010.

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Particulate Proficiency Testing Scheme, Round 3

by

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1. INTRODUCTION

This report describes the results of the third round of a particulate measurement proficiency-testing scheme carried out by the National Physical Laboratory.

The particulate 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 companies took part in the third 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 12 mg. The shims had nominal masses in the range 140 mg to 920 mg. Three shim sizes were on offer to participants, the masses of which chosen to mimic the mass of typical 47mm, 83mm and 110mm quartz fibre filters used in the stack emissions measurement industry.

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 particulate procedure in accordance with BS EN 13284-1. 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 particulate 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 evaporated by participants following their standard methodology and weighed, again in accordance with BS EN 13284-1. The mass of particulate in the washing solution should equal the 11.9mg known to be in the solutions provided to the participants.

The results of these analyses were returned to 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 2, and a summary of the results is also given in Table 1 and 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.

$$z = \frac{x - T}{\sigma}$$ 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:

$-2 \geq \lvert z \rvert \leq 2$	satisfactory
$-3 > \lvert z \rvert < -2$ or $2 > \lvert z \rvert < 3$	questionable
$\lvert z \rvert \leq -3$ or $\lvert z \rvert \geq 3$	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 the shim element of the scheme has been selected as 0.1 mg, this has been chosen to be 10% of a 1 mg particulate loading. The value of σ used for the washings element of the scheme has been selected as 2.38 mg; 20% of the assigned value. This relatively lenient target standard deviation has been chosen because of the additional complexity of required to measure a washing solution.

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

Participant results for the shim masses are presented in Table 1, 2 and 3 along with shim assigned values and uncertainties.

Company I/D	Shim ID	Shim AV (mg)	Reported Shim Weight (mg)	Shim AV Uncertainty (mg)	Deviation from AV (mg)
1	14	155.63	155.62	0.003	-0.01
2	3	142.26	142.24	0.003	-0.02
3	13	147.08	147.08	0.003	0.00
4	15	151.30	151.40	0.003	0.10
5	8	147.07	147.04	0.003	-0.03
8	20	139.85	139.90	0.003	0.05
9	27	146.35	146.32	0.003	-0.03
10	5	145.64	145.66	0.003	0.02
11	11	144.47	144.49	0.003	0.02
12	25	155.30	155.29	0.003	-0.01
13	9	149.18	149.30	0.003	0.12
15	1	153.60	153.65	0.003	0.05
16	23	150.35	150.30	0.003	-0.05
17	16	147.82	148.00	0.003	0.18
18	28	144.73	144.72	0.003	-0.01
20	6	149.75	149.77	0.003	0.02
21	18	151.03	151.10	0.003	0.07
22	26	140.96	140.83	0.003	-0.13
26	2	141.56	141.56	0.003	0.00

27	22	146.60	146.60	0.003	0.00
29	7	155.07	155.12	0.003	0.05
30	12	146.96	146.98	0.003	0.02
31	21	143.54	143.53	0.003	-0.01
32	4	148.11	148.10	0.003	-0.01
33	19	148.98	149.00	0.003	0.02
34	17	145.52	145.57	0.003	0.05
35	24	152.46	152.39	0.003	-0.07
36	10	146.97	146.97	0.003	0.00

Table 1. Difference, in mg, between reported results and NPL assigned value for 47mm shim

Company I/D	Shim ID	Shim AV (mg)	Reported Shim Weight (mg)	Shim AV Uncertainty (mg)	Deviation from AV (mg)
2	37	394.34	394.38	0.005	0.04
4	38	384.59	384.60	0.005	0.01
6	40	417.62	417.60	0.005	-0.02
21	39	416.24	416.30	0.005	0.06
28	36	403.66	403.71	0.005	0.05
35	41	408.01	408.08	0.005	0.07

Table 2. Difference, in mg, between reported results and NPL assigned value for 83mm shim

Company I/D	Shim ID	Shim AV (mg)	Reported Shim Weight (mg)	Shim AV Uncertainty (mg)	Deviation from AV (mg)
19	47	915.95	915.93	0.005	-0.02

21	49	902.60	902.60	0.005	0.00
24	46	914.12	914.10	0.005	-0.02
29	48	906.09	906.07	0.005	-0.02
35	50	910.33	910.53	0.005	0.20

Table 3. Difference, in mg, between reported results and NPL assigned value for 110mm shim

The agreement with the assigned absolute shim masses is 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 across all shim sizes is 0.06 mg, this provides an indication of the variability of particulate across the participants. The average difference in milligrams is 0.02 mg, which shows excellent agreement with the known masses and no significant bias in the results.

The z score results for the shim measurements are given in Table 4, 5 and 6.

Company I/D	Shim ID	% Difference from AV	Z Score
1	14	-0.01	-0.10
2	3	-0.01	-0.20
3	13	0.00	0.03
4	15	0.07	1.00
5	8	-0.02	-0.27
8	20	0.04	0.50
9	27	-0.02	-0.33
10	5	0.01	0.20
11	11	0.01	0.20
12	25	-0.01	-0.10
13	9	0.08	1.23

15	1	0.03	0.50
16	23	-0.03	-0.50
17	16	0.12	1.83
18	28	-0.01	-0.13
20	6	0.02	0.23
21	18	0.05	0.70
22	26	-0.09	-1.30
26	2	0.00	0.03
27	22	0.00	0.04
29	7	0.03	0.50
30	12	0.01	0.20
31	21	-0.01	-0.10
32	4	-0.01	-0.10
33	19	0.01	0.20
34	17	0.04	0.53
35	24	-0.04	-0.67
36	10	0.00	0.00

Table 4. 47mm shim results, percentage difference and z scores

Company I/D	Shim ID	% Difference from AV	Z Score
2	37	0.01	0.43
4	38	0.00	0.10
6	40	0.00	-0.20

21	39	0.01	0.57
28	36	0.01	0.50
35	41	0.02	0.70

Table 5. 83mm shim results, percentage difference and z scores

Company I/D	Shim ID	% Difference from AV	Z Score
29	48	0.00	-0.20
35	50	0.02	2.00
24	46	0.00	-0.20
19	47	0.00	-0.17
21	49	0.00	0.00

Table 6. 110mm shim results, percentage difference and z scores

The z score results for the shims are good, with only one participant with a z-score greater/less than +/-2. Figures 1, 2, 3, 4, 5 and 6 show these results graphically.

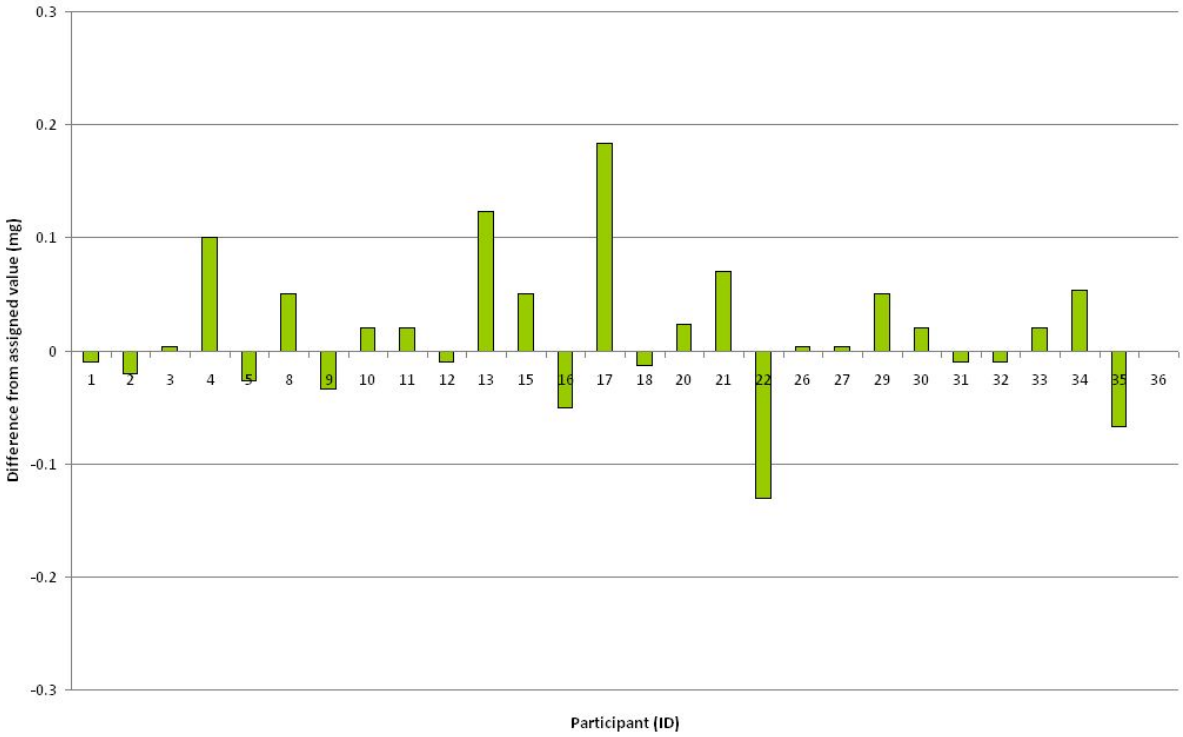

Figure 1. Difference in 47mm shim mass from assigned values

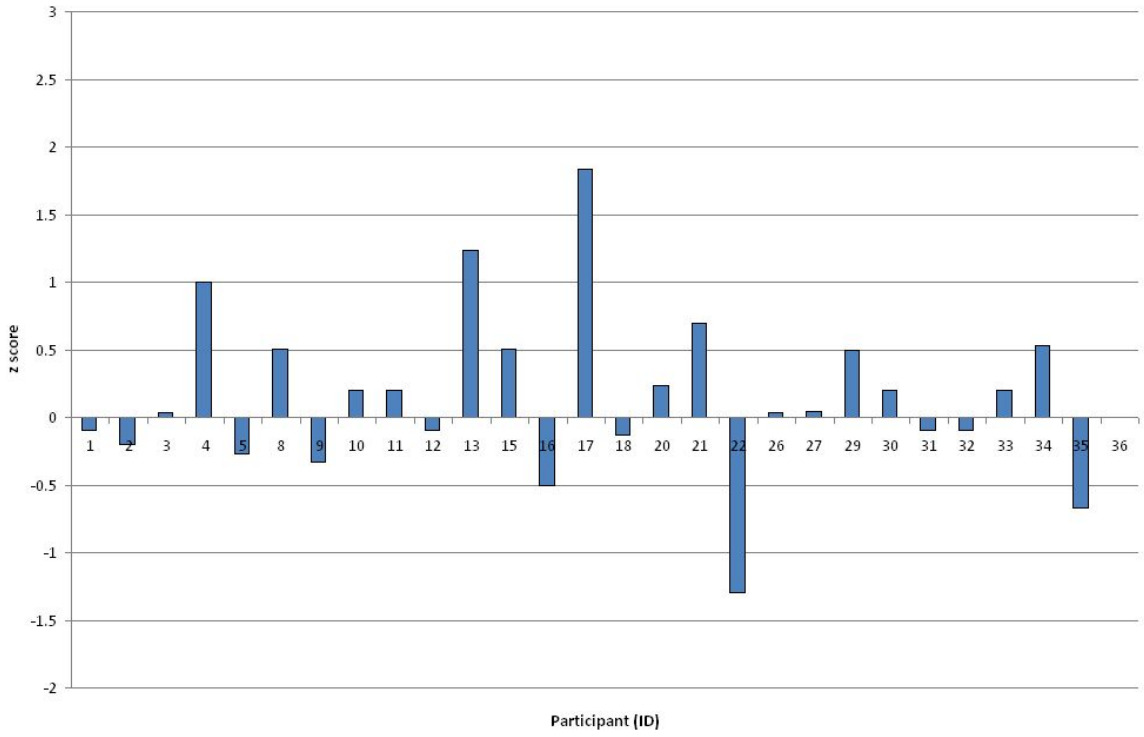

Figure 2. z scores for 47mm shims, σ = 0.1mg

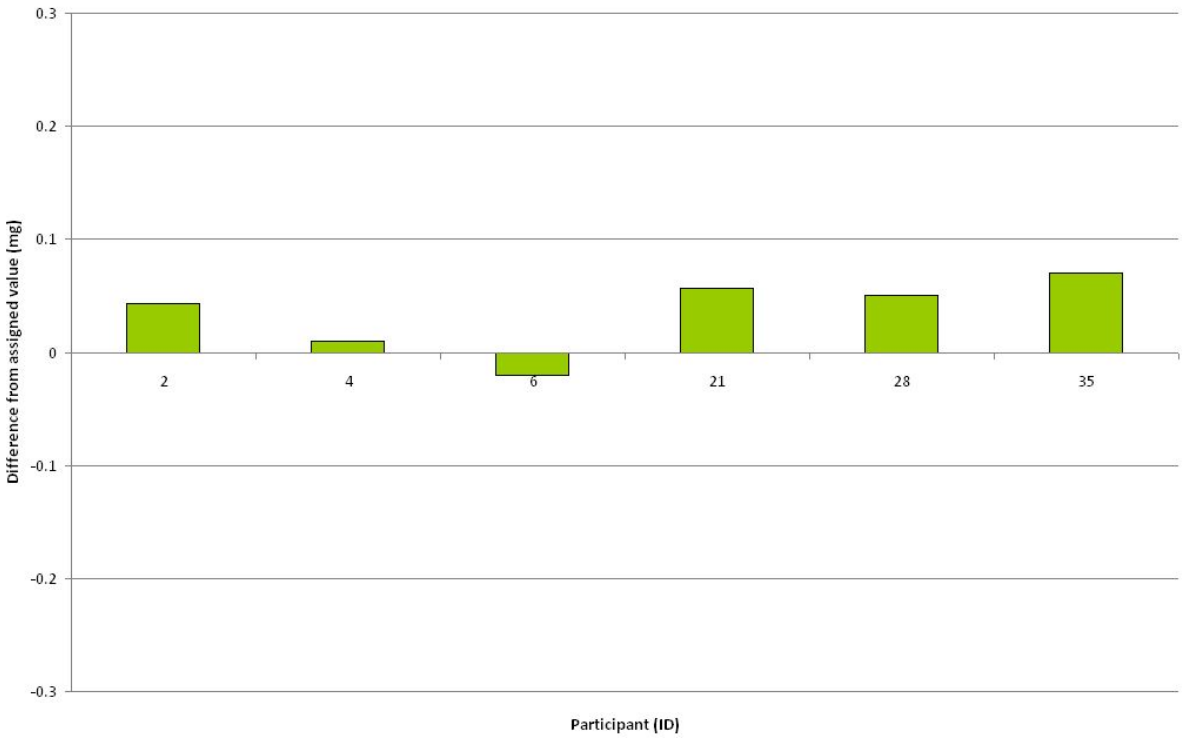

Figure 3. Difference in 83mm shim mass from assigned values

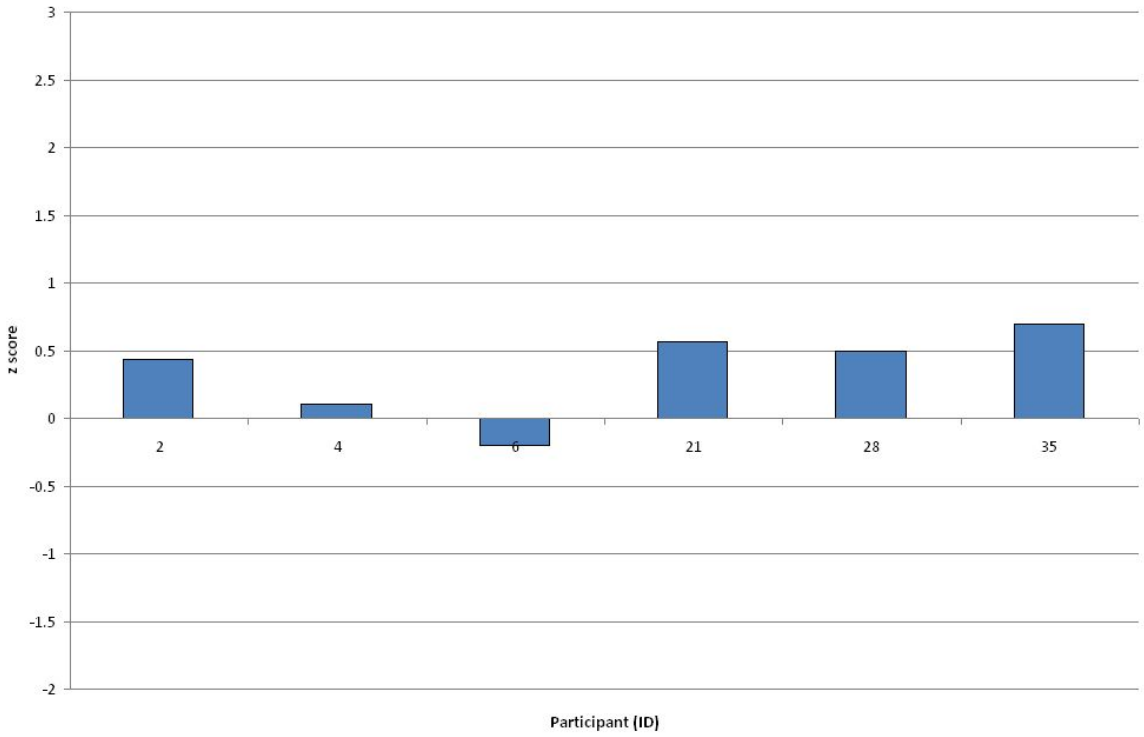

Figure 4. z scores for 83mm shims, σ = 0.1mg

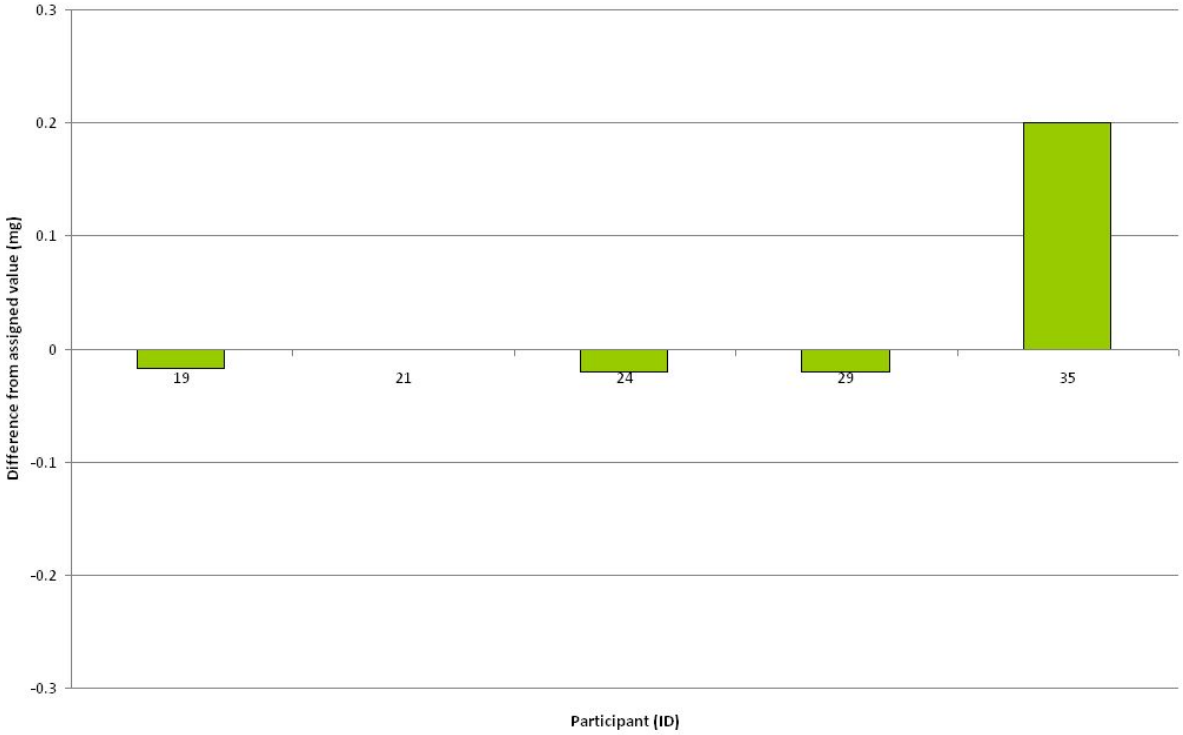

Figure 5. Difference in 110mm shim mass from assigned values

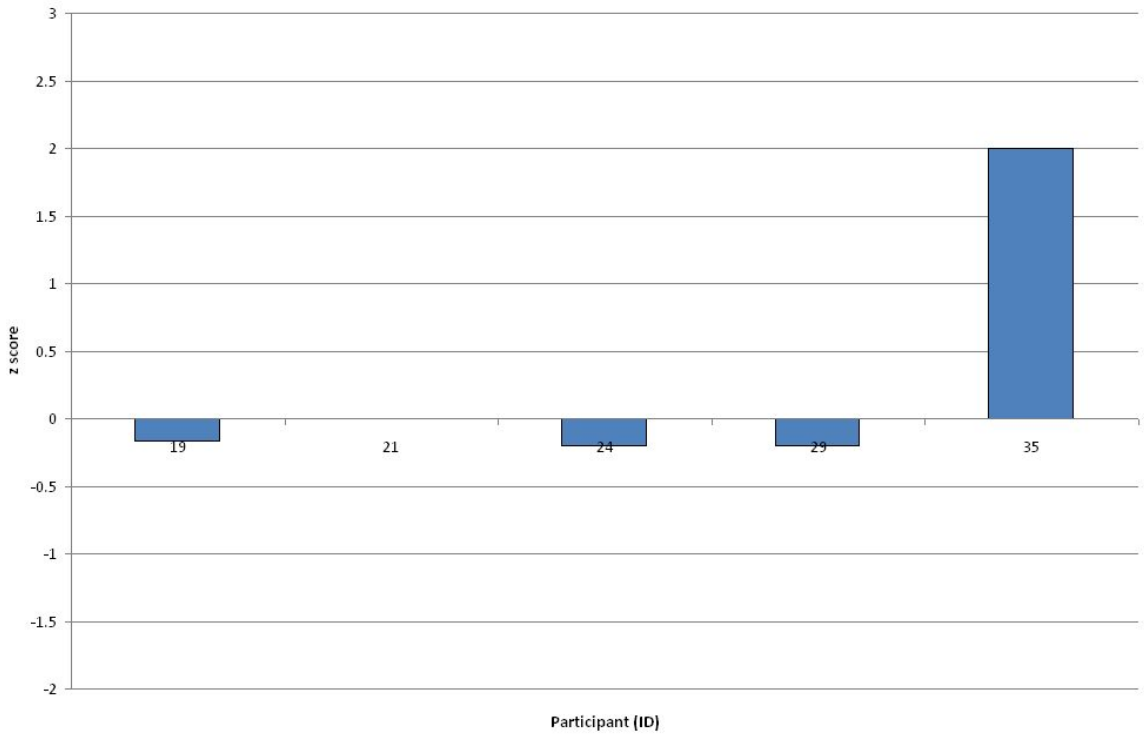

Figure 6. z scores for 110mm shims, σ = 0.1mg

The results for the solution evaporation and particulate are given in Table 7. This gives the results from the evaporation of the washing solution by participants and the deviation from the assigned value. The total mass of residue should be equal to the 11.9mg salt present in the provided samples.

Company I/D	Washing AV (mg)	Washing AV Uncertainty (mg)	Reported Wash Weight (mg)	Deviation from AV (mg)
1	11.90	0.18	11.51	-0.39
2	11.90	0.18	11.91	0.01
3	11.90	0.18	9.30	-2.60
4	11.90	0.18	11.20	-0.70
5	11.90	0.18	11.94	0.04
6	11.90	0.18	11.50	-0.40
8	11.90	0.18	12.10	0.20
9	11.90	0.18	13.75	1.85
10	11.90	0.18	11.00	-0.90
11	11.90	0.18	11.70	-0.20
12	11.90	0.18	11.99	0.09
13	11.90	0.18	10.20	-1.70
15	11.90	0.18	11.92	0.02
16	11.90	0.18	9.20	-2.70
17	11.90	0.18	9.80	-2.10
18	11.90	0.18	10.37	-1.53
19	11.90	0.18	12.70	0.80
20	11.90	0.18	12.07	0.17
21	11.90	0.18	10.90	-1.00

22	11.90	0.18	11.02	-0.88
24	11.90	0.18	10.01	-1.89
26	11.90	0.18	0.89	-11.01
27	11.90	0.18	11.80	-0.10
28	11.90	0.18	13.61	1.71
29	11.90	0.18	11.78	-0.12
30	11.90	0.18	11.80	-0.10
31	11.90	0.18	12.01	0.11
32	11.90	0.18	12.60	0.70
33	11.90	0.18	12.00	0.10
34	11.90	0.18	10.54	-1.36
35	11.90	0.18	11.26	-0.64
36	11.90	0.18	13.00	1.10

Table 7. Difference, in mg, between reported washing results and NPL assigned value

Table 8 presents the washing solution results as percentage difference from the assigned value and as a z-score with a target standard deviation of 2.38 mg.

Company I/D	% Difference from AV	Z Score
1	-3.28	-0.16
2	0.08	0.00
3	-21.85	-1.09
4	-5.88	-0.29
5	0.34	0.02

6	-3.36	-0.17
8	1.68	0.08
9	15.55	0.78
10	-7.56	-0.38
11	-1.68	-0.08
12	0.76	0.04
13	-14.29	-0.71
15	0.17	0.01
16	-22.69	-1.13
17	-17.65	-0.88
18	-12.86	-0.64
19	6.72	0.34
20	1.43	0.07
21	-8.40	-0.42
22	-7.39	-0.37
24	-15.88	-0.79
26	-92.52	-4.63
27	-0.84	-0.04
28	14.37	0.72
29	-1.01	-0.05
30	-0.84	-0.04
31	0.92	0.05

32	5.88	0.29
33	0.84	0.04
34	-11.43	-0.57
35	-5.38	-0.27
36	9.24	0.46

Table 8. Washing solutions, percentage differences and z scores

Figures 7 and 8 present the percentage difference and z-scores for the washing solution results.

The z-score for the solution evaporation and particulate results has been calculated using a target standard deviation, σ, of 2.38 mg. Despite this relatively conservative target (equivalent to 20% of the assigned value of 11.9 mg), the results are variable, with one participant gaining a z-score in excess of +/-3. The standard deviation of the differences from the expected weights was 2.17 mg, which is close to the assigned 2.38 mg standard deviation.

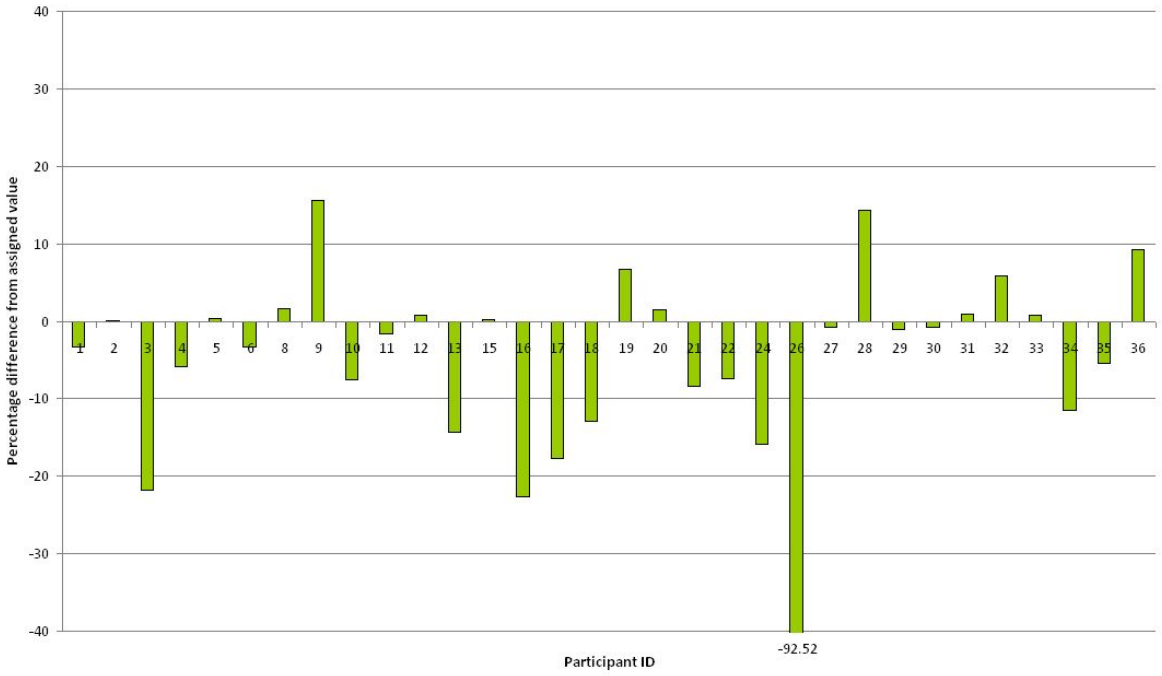

Figure 7. Percentage Difference in washing solution residual weight from assigned values

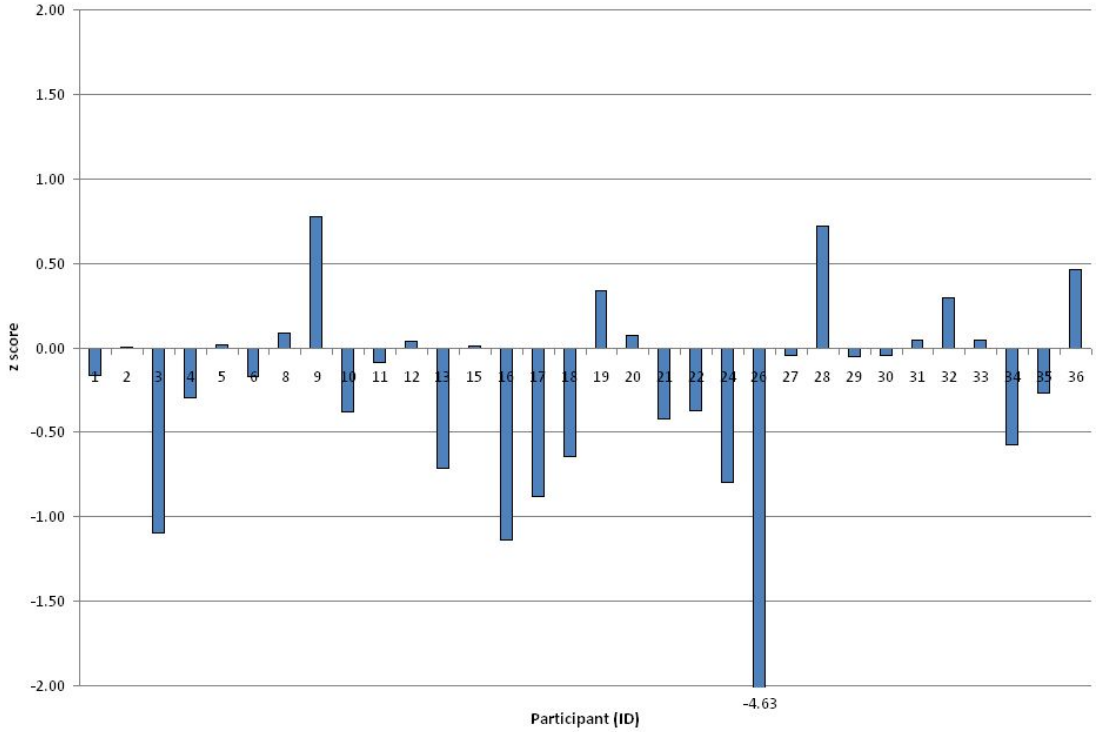

Figure 8. Washing Solution residue z score, σ = 2.38mg

4. ROUND COMPARISON

This is the third round of the particulate proficiency testing scheme. Further rounds of the scheme will enable us to look for trends in results and enable participants to judge their performance year on year. Table 9 and 10 give the percentage of participants in each of the z score performance bands for shim weighing and washings analysis. For the shim weighing element of the scheme performance has been consistently excellent with no participants falling outside of the $-2 \geq |z| \leq 2$ range in the last round. For the washings element of the scheme performance has been much more varied. However table 10 shows an improvement in z scores over the three rounds of the scheme which is very encouraging.

	Round 1	Round 2	Round 3
$-2 \geq \|z\| \leq 2$	97	97	100
$-3 > \|z\| < -2$ or $2 > \|z\| < 3$	3	3	0
$\|z\| \leq -3$ or $\|z\| \geq 3$	0	0	0

Table 9. Percentage of participants in each z score performance band for last three rounds of shim weighing.

	Round 1	Round 2	Round 3
$-2 \geq \|z\| \leq 2$	74	89	97
$-3 > \|z\| < -2$ or $2 > \|z\| < 3$	6	11	0
$\|z\| \leq -3$ or $\|z\| \geq 3$	19	0	3

Table 10. Percentage of participants in each z score performance band for the last three rounds of washings analysis.

5. CONCLUSIONS

The results from the shim measurements are generally encouraging and indicate that most labs have their balances under calibration. Only one laboratory achieved an unacceptable z score for the washings. The laboratory in question did not have a problem with the shim weighing element of the scheme indicating a problem with sample handling rather than balance calibration. There were no questionable or unsatisfactory results for the shim weighing.

The results from the washings solution are much more encouraging and shown significant improvement year on year. All labs bar one achieved a z score less than 3 in this round. Removing the outlier with a z score in excess of 3 the standard deviation of the differences from the expected weights was 1.11 mg with an average of –0.40 mg.