

Calibration Gas Proficiency Testing Scheme Round 4

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ABSTRACT

This report presents the results from the fourth round of the calibration gas proficiency testing scheme operated by NPL for the STA.

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Approved on behalf of NPLML by Martyn Sene, Director of Operations, *Operations
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CONTENTS

1	INTRODUCTION	1
2	PROFICIENCY TESTING SCHEME DESCRIPTION	2
2.1	ORGANISATION	2
2.2	DATA ANALYSIS.....	2
3	RESULTS.....	5
4	DISCUSSION.....	17
4.1	SO ₂	17
4.2	CO.....	17
4.3	NO.....	17
4.4	O ₂	17
4.5	C ₃ H ₈	17
4.6	UNCERTAINTIES.....	17
4.7	CYLINDER CHECK.....	17

1 INTRODUCTION

This report describes the results of the fourth round of a calibration gas proficiency-testing scheme carried out by the National Physical Laboratory for the Source Testing Association. Measurements were made on sets of seven cylinders circulated to participants in a 'round robin'. There were three sets of test gases therefore not all participants measured the same cylinders.

The calibration gas Proficiency Testing (PT) scheme provides a way of assessing the performance of laboratories by a series of regular inter-laboratory comparisons. The assigned values were provided by traceable measurements of the concentrations of the gases carried out by NPL and Cryoservice. The results of each participant's analyses were compared to assigned values of the test gases. 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 PROFICIENCY TESTING SCHEME DESCRIPTION

2.1 ORGANISATION

Thirty-six companies took part in the fourth round of the scheme, which involved the measurement of a number of traceable standard gas mixtures sent round to participants' laboratories.

The PT scheme assesses the measurement of gaseous components using continuous emission monitoring (CEM) equipment. This has the benefit that the test samples each have a known, 'true' value, and that the analysis of these is non destructive, in the sense that the same gas mixture can be analysed by more than one laboratory. The list of species and nominal concentrations of the gas mixtures used in this round of the PT scheme is given in Table 1.

Table 1 Gases used in round 5 of the calibration gas proficiency testing scheme

Species	Nominal Concentration
SO ₂	1000 ppm
SO ₂	100 ppm
CO	1000 ppm
CO	100 ppm
NO	500 ppm
O ₂	11 %
C ₃ H ₈	10 ppm

The participants were told the nominal concentration of the cylinders they received as given in Table 1, but not the absolute value. The results of these analyses were returned to NPL. Participants were also requested to report the measurement uncertainty that they assigned to the results obtained. Not all participants took part in all tests and not all reported uncertainties.

Participants were requested to inject the test gases into the end of the sample probe of their gas analyser including all gas conditioning/filtration systems where these would normally be used.

2.2 DATA ANALYSIS

Participants were requested to make a single measurement of each test gas. Each measurement is expressed as a percentage difference from the assigned value. Using this method it is left up to the participant to judge 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 from analyses of the same sample and with analyses of different species. If a suitable value of σ is chosen for each

species 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:

$-2 \leq z \leq 2$	satisfactory
$-3 < z < -2$ or $2 < z < 3$	questionable
$z \leq -3$ or $z \geq 3$	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 the fourth round of the PT Scheme is shown in table 2. The value of σ has been chosen with reference to the results from previous rounds, the relevant CEN standards, the Waste Incineration Directive (WID) and the Large Combustion Plant Directive (LCPD).

Table 2 Standard deviation for proficiency testing

Species	Nominal concentration	Standard deviation for proficiency testing
SO ₂	1000 ppm	36.9 ppm
SO ₂	100 ppm	2.7 ppm
CO	1000 ppm	32.1 ppm
CO	100 ppm	2.9 ppm
NO	500 ppm	23.9 ppm
O ₂	11 %	0.17 %
C ₃ H ₈	10 ppm	0.34 ppm

A z score of 2 or greater shows significant bias in the measured result which is probably not due to random variability. 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.

The assigned values and their uncertainties are shown in Table 3.

Table 3 Assigned values and their uncertainties

Species	Nominal concentration	Cylinder number	Cylinder set	Assigned value (AV)	Standard uncertainty (k=2)
SO ₂	1000 ppm	P2851ZD773525	A	1004	20
SO ₂	1000 ppm	P2602L260A	C	1010	20
SO ₂	1000 ppm	P2851ZD773494	B	1008	20
SO ₂	1000 ppm	P2851ZD616608	D	1041	21
SO ₂	100 ppm	P2602L1029A	A	99.4	2.0
SO ₂	100 ppm	P2851ZD655314	B	101.0	2.0
SO ₂	100 ppm	P2851ZD102970	C	99.6	2.0
SO ₂	100 ppm	P2851ZD616606	D	102.8	2.1
CO	1000 ppm	P2851ZMZ0613	A	943	18.9
CO	1000 ppm	P2851ZMZ0492	B	949	19.0
CO	1000 ppm	P2602L1123A	C	957	19.1
CO	100 ppm	P2602L82A	A	86.4	1.7
CO	100 ppm	P2602L1564A	B	86.8	1.7
CO	100 ppm	P2851ZMN8557	C	86.9	1.7
NO	500 ppm	P2851ZD4245	C	439	9
NO	500 ppm	P2851ZD291478	A	438	9
NO	500 ppm	P2851ZD616636	B	454	9
O ₂	11 %	P2851ZD909557	A	11.12	0.22
O ₂	11 %	P2851ZD4342	B	11.07	0.22
O ₂	11 %	P2851ZMZ0570	C	11.07	0.22
C ₃ H ₈	10 ppm	P2851ZD709310	C	9.00	0.18
C ₃ H ₈	10 ppm	P2602L2227A	A	9.30	0.19
C ₃ H ₈	10 ppm	P2851ZD395934	B	9.00	0.18

3 RESULTS

The difference, percentage difference and z scores for each species are show in Table 4 to 8.

Table 4 Proficiency test results for 1000 ppm SO₂

Participant	Submitted result (ppm)	Difference from AV (ppm)	% Difference from AV	Z score
1	1007	-3	-0.30	-0.08
2	1275	265	26.24	7.18
3	1017.46	7.46	0.74	0.20
4	997	-13	-1.29	-0.35
5	998.9	-11.1	-1.10	-0.30
6	1035.78	25.78	2.55	0.70
7				
8	1008	-2	-0.20	-0.05
9	1050.7	40.7	4.03	1.10
10				
11	1013	5	0.50	0.14
12	998	-6	-0.60	-0.16
13	1019	11	1.09	0.30
14	1035.9	27.9	2.77	0.76
15	950	-58	-5.75	-1.57
16	1023	19	1.89	0.51
17	992	-12	-1.20	-0.33
18	1008	4	0.40	0.11
19	1021	13	1.29	0.35
20				
21	1008	4	0.40	0.11
22	995	-13	-1.29	-0.35
23	1062.34	58.34	5.81	1.58
24	1042.8	1.8	0.17	0.05
25				
26	1025	-16	-1.54	-0.43
27	1022	18	1.79	0.49
28	1032	-9	-0.86	-0.24
29	996.7	-13.3	-1.32	-0.36
30	1055	45	4.46	1.22
31				
32	1024	14	1.39	0.38
33	1079	69	6.83	1.87
34				
35	1017	-24	-2.31	-0.65
36	1038	-3	-0.29	-0.08

Table 5 Proficiency test results for 100 ppm SO₂

Participant	Submitted result (ppm)	Difference from AV (ppm)	% Difference from AV	Z score
1	98.9	-0.7	-0.70	-0.26
2	118	18.4	18.47	6.81
3	104.04	4.44	4.46	1.64
4	117.9	18.3	18.37	6.78
5	99.8	0.2	0.20	0.07
6	102.44	2.84	2.85	1.05
7				
8	96	-3.6	-3.61	-1.33
9	98.53	-1.07	-1.07	-0.40
10				
11	103.6	2.6	2.57	0.96
12	100.5	1.1	1.11	0.41
13	95	-6	-5.94	-2.22
14	102.3	1.3	1.29	0.48
15	91	-10	-9.90	-3.70
16	98.6	-0.8	-0.80	-0.30
17	97.3	-2.1	-2.11	-0.78
18	96	-3.4	-3.42	-1.26
19	19	0.4	0.40	0.15
20	110.4	10.8	10.84	4.00
21	96	-3.4	-3.42	-1.26
22	96	-5	-4.95	-1.85
23	99.87	0.47	0.47	0.17
24	101.2	-1.6	-1.56	-0.59
25				
26	100	-2.8	-2.72	-1.04
27	106	6.6	6.64	2.44
28	103.7	0.9	0.88	0.33
29	99.9	0.5	0.50	0.19
30	102	2.4	2.41	0.89
31				
32	100.1	0.7	0.70	0.26
33	100.7	1.3	1.31	0.48
34				
35	96.4	-6.4	-6.23	-2.37
36	101	-1.8	-1.75	-0.67

Table 6 Proficiency test results for 1000 ppm CO

Participant	Submitted result (ppm)	Difference from AV (ppm)	% Difference from AV	Z score
1	950	-7	-0.73	-0.22
2	934	-23	-2.40	-0.72
3	884	-73	-7.63	-2.27
4	957	0	0.00	0.00
5	922.8	-34.2	-3.57	-1.07
6	978.62	21.62	2.26	0.67
7	946	-11	-1.15	-0.34
8	960	3	0.31	0.09
9	984	27	2.82	0.84
10	952	-5	-0.52	-0.16
11	961	12.3	1.30	0.38
12	940	-2.9	-0.31	-0.09
13	996	47.3	4.99	1.47
14	949.7	1	0.11	0.03
15	959	10.3	1.09	0.32
16	947	4.1	0.43	0.13
17	935	-7.9	-0.84	-0.25
18	941	-1.9	-0.20	-0.06
19	19	-0.7	-0.07	-0.02
20	1010	53	5.54	1.65
21	941	-1.9	-0.20	-0.06
22				
23	969.02	26.12	2.77	0.81
24	956.9	8.2	0.86	0.26
25	940	-2.9	-0.31	-0.09
26	952	3.3	0.35	0.10
27	939	-3.9	-0.41	-0.12
28	951	2.3	0.24	0.07
29	946.2	3.3	0.35	0.10
30	959	2	0.21	0.06
31	959	2	0.21	0.06
32	959	16.1	1.71	0.50
33	963.3	20.4	2.16	0.64
34	960.39	17.49	1.85	0.54
35	975.7	27	2.85	0.84
36	958	9.3	0.98	0.29

Table 7 Proficiency test results for 100 ppm CO

Participant	Submitted result (ppm)	Difference from AV (ppm)	% Difference from AV	Z score
1	84.5	-2.4	-2.76	-0.83
2	81.5	-5.4	-6.21	-1.86
3	89.07	2.17	2.50	0.75
4	88.3	1.4	1.61	0.48
5	86.2	-0.7	-0.81	-0.24
6	88.61	1.71	1.97	0.59
7	89.9	3	3.45	1.03
8	90	3.1	3.57	1.07
9	88.07	1.17	1.35	0.40
10	92.9	6	6.90	2.07
11	87.3	0.5	0.58	0.17
12	87.2	0.8	0.93	0.28
13	85	-1.8	-2.07	-0.62
14	89.4	2.6	3.00	0.90
15	86	-0.8	-0.92	-0.28
16	86.3	-0.1	-0.12	-0.03
17	96.4	10	11.57	3.45
18	87.7	1.3	1.50	0.45
19	19	0.7	0.81	0.24
20	98.6	11.7	13.46	4.03
21	87.7	1.3	1.50	0.45
22	84	-2.8	-3.23	-0.97
23	86.91	0.51	0.59	0.18
24	87.1	0.3	0.35	0.10
25	87.3	0.9	1.04	0.31
26	84.5	-2.3	-2.65	-0.79
27	89.2	2.8	3.24	0.97
28	88.6	1.8	2.07	0.62
29	86.3	-0.1	-0.12	-0.03
30	87	0.1	0.12	0.03
31	85.45	-1.45	-1.67	-0.50
32	86.2	-0.2	-0.23	-0.07
33	85.3	-1.1	-1.27	-0.38
34	95.09	8.69	10.06	3.00
35	93.9	7.1	8.18	2.45
36	87	0.2	0.23	0.07

Table 8 Proficiency test results for 500 ppm NO

Participant	Submitted result (ppm)	Difference from AV (ppm)	% Difference from AV	Z score
1	455.4	16.8	3.83	0.70
2	457	18.4	4.20	0.77
3	451.42	12.82	2.92	0.54
4	444.6	6	1.37	0.25
5	430.2	-8.4	-1.92	-0.35
6	434.06	-4.54	-1.04	-0.19
7	439	0.4	0.09	0.02
8	448	9.4	2.14	0.39
9	426.7	-11.9	-2.71	-0.50
10	474	35.4	8.07	1.48
11	467.1	13.3	2.93	0.56
12	439	0.9	0.21	0.04
13	454	0.2	0.04	0.01
14	478.8	25	5.51	1.05
15	455	1.2	0.26	0.05
16	444	5.9	1.35	0.25
17	435	-3.1	-0.71	-0.13
18	439	0.9	0.21	0.04
19	19	1.2	0.26	0.05
20	467.4	28.8	6.57	1.21
21	439	0.9	0.21	0.04
22	447	-6.8	-1.50	-0.28
23	459.16	21.06	4.81	0.88
24	457.2	3.4	0.75	0.14
25	384	-54.1	-12.35	-2.26
26	450	-3.8	-0.84	-0.16
27	457	18.9	4.31	0.79
28	466.7	12.9	2.84	0.54
29	462.7	24.6	5.62	1.03
30	448	9.4	2.14	0.39
31	439.5	0.9	0.21	0.04
32	437	-1.1	-0.25	-0.05
33	423.6	-14.5	-3.31	-0.61
34	437.11	-0.99	-0.23	-0.04
35	443.4	-10.4	-2.29	-0.44
36	455	1.2	0.26	0.05

Table 9 Proficiency test results for 11 % O₂

Participant	Submitted result (ppm)	Difference from AV (ppm)	% Difference from AV	Z score
1	11.09	0.016	0.14	0.09
2	10.97	-0.104	-0.94	-0.61
3	11.11	0.036	0.33	0.21
4	11.15	0.076	0.69	0.45
5	11.09	0.016	0.14	0.09
6	11.02	-0.054	-0.49	-0.32
7	11.09	0.016	0.14	0.09
8	11.16	0.086	0.78	0.51
9	11.09	0.016	0.14	0.09
10	11.13	0.056	0.51	0.33
11	11.07	-0.003	-0.03	-0.02
12	11.17	0.046	0.41	0.27
13	11.17	0.097	0.88	0.57
14	11.1	0.027	0.24	0.16
15	11.12	0.047	0.42	0.28
16	11.1	-0.024	-0.22	-0.14
17	11.11	-0.014	-0.13	-0.08
18	11.1	-0.024	-0.22	-0.14
19	11.05	-0.023	-0.21	-0.14
20	9.01	-2.064	-18.64	-12.14
21	11.1	-0.024	-0.22	-0.14
22	11.11	0.037	0.33	0.22
23	11.98	0.856	7.70	5.04
24	11.1	0.027	0.24	0.16
25	11.23	0.106	0.95	0.62
26	11.2	0.127	1.15	0.75
27	11.17	0.046	0.41	0.27
28	11.24	0.167	1.51	0.98
29	11.14	0.016	0.14	0.09
30	11.62	0.546	4.93	3.21
31	11.07	-0.004	-0.04	-0.02
32	11.45	0.326	2.93	1.92
33	11.16	0.036	0.32	0.21
34	11.19	0.066	0.59	0.39
35	11.32	0.247	2.23	1.45
36	11.02	-0.053	-0.48	-0.31

Table 10 Proficiency test results for 10 ppm C₃H₈

Participant	Submitted result (ppm)	Difference from AV (ppm)	% Difference from AV	Z score
1	6.4	-2.6	-28.89	-7.65
2	5.6	-3.4	-37.78	-10.00
3	8.66	-0.34	-3.78	-1.00
4	9.92	0.92	10.22	2.71
5	8.6	-0.4	-4.44	-1.18
6	8.68	-0.32	-3.56	-0.94
7	9.1	0.1	1.11	0.29
8				
9				
10	8.95	-0.05	-0.56	-0.15
11	9.2	0.2	2.22	0.59
12	9.2	-0.1	-1.08	-0.29
13	8.6	-0.4	-4.44	-1.18
14	6.94	-2.06	-22.89	-6.06
15	8.4	-0.6	-6.67	-1.76
16	9.3	0	0.00	0.00
17	9.3	0	0.00	0.00
18	9.3	0	0.00	0.00
19	19	-0.5	-5.56	-1.47
20	8.7	-0.3	-3.33	-0.88
21	9.3	0	0.00	0.00
22	9.1	0.1	1.11	0.29
23	9.11	-0.19	-2.04	-0.56
24	8.98	0	0.00	0.00
25	10.9	1.6	17.20	4.71
26	9	0	0.00	0.00
27	9.13	-0.17	-1.83	-0.50
28				
29	9.3	0	0.00	0.00
30	8.9	-0.1	-1.11	-0.29
31				
32	10.4	1.1	11.83	3.24
33				
34	8.66	-0.64	-6.88	-1.88
35	8.9	-0.1	-1.11	-0.29
36	8.35	-0.65	-7.22	-1.91

Figures 1 to 7 illustrate the % difference between the assigned value and the submitted result with error bars showing the measurement uncertainty attributed by each participant. Figures 8 and 9 summarise the z scores for all participants and species.

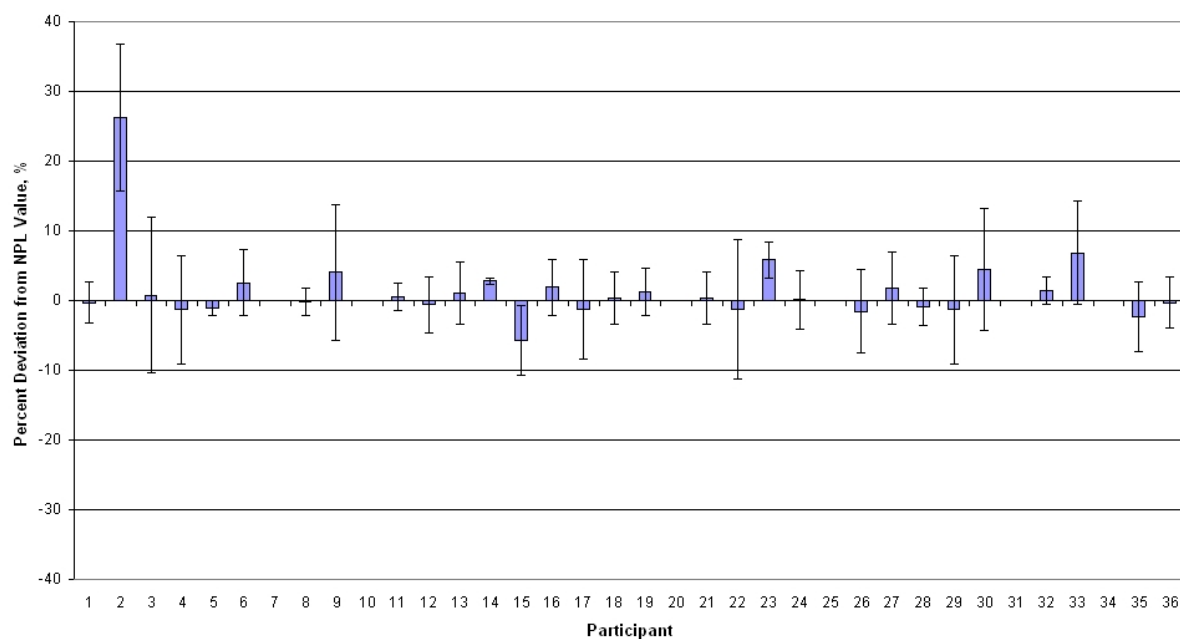


Figure 1
1000 ppm SO₂ percentage difference from assigned value and uncertainty error bars attributed by participants

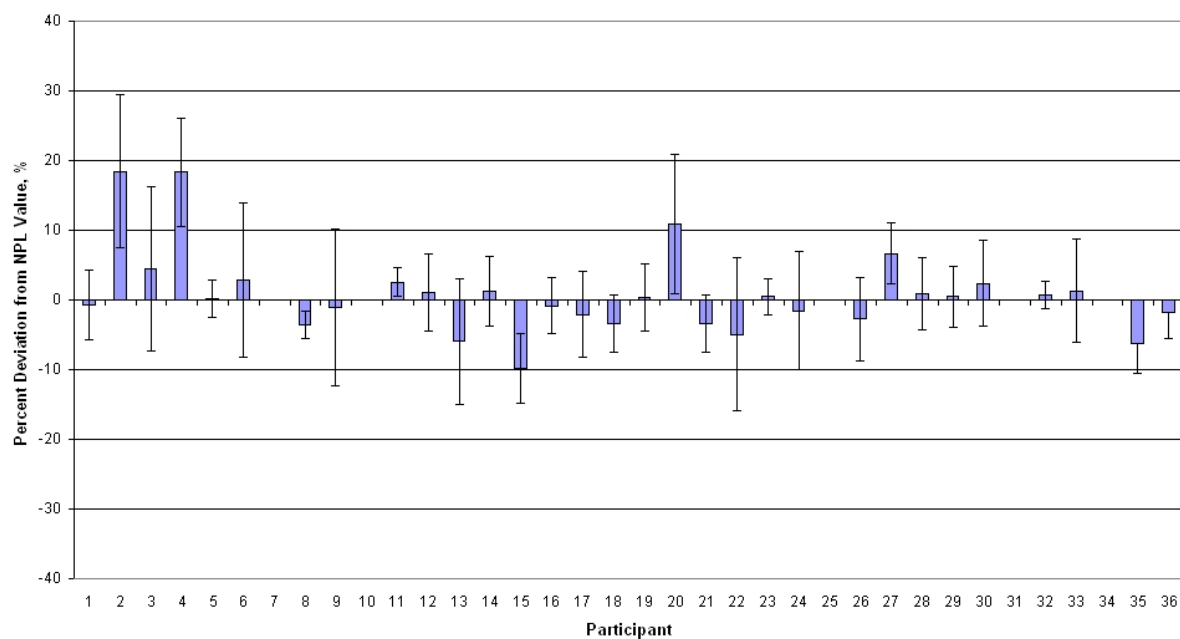


Figure 2
100 ppm SO₂ percentage difference from assigned value and uncertainty error bars attributed by participants

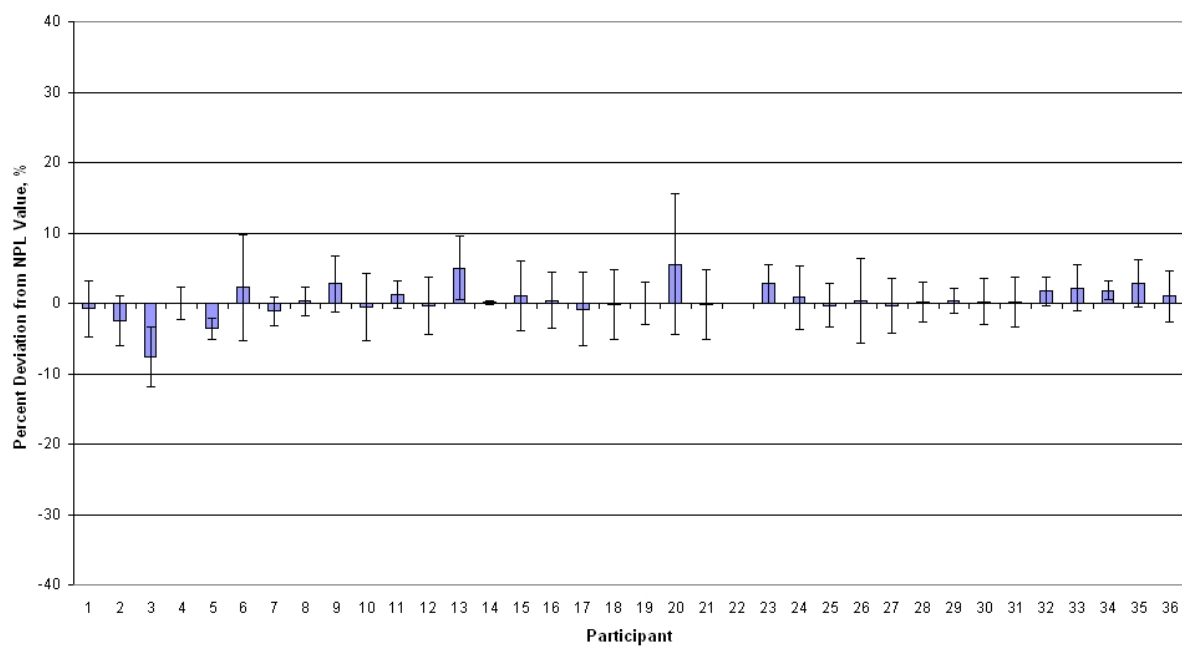


Figure 3
1000 ppm CO percentage difference from assigned value and uncertainty error bars
attributed by participants

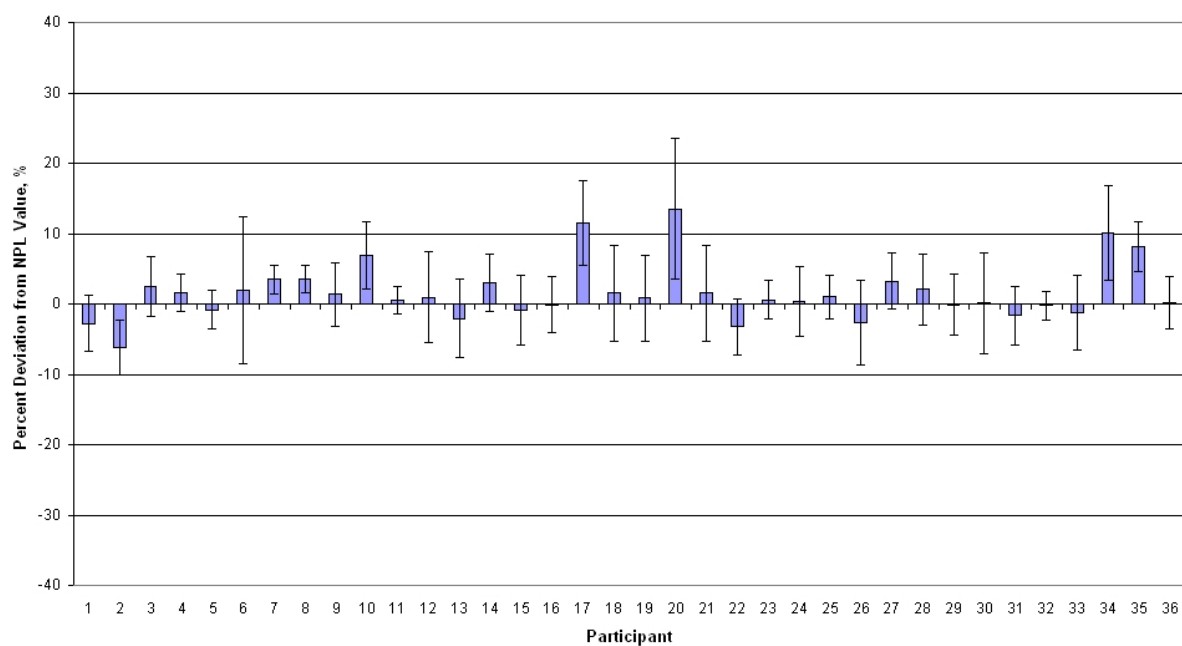


Figure 4
100 ppm CO percentage difference from assigned value and uncertainty error bars
attributed by participants

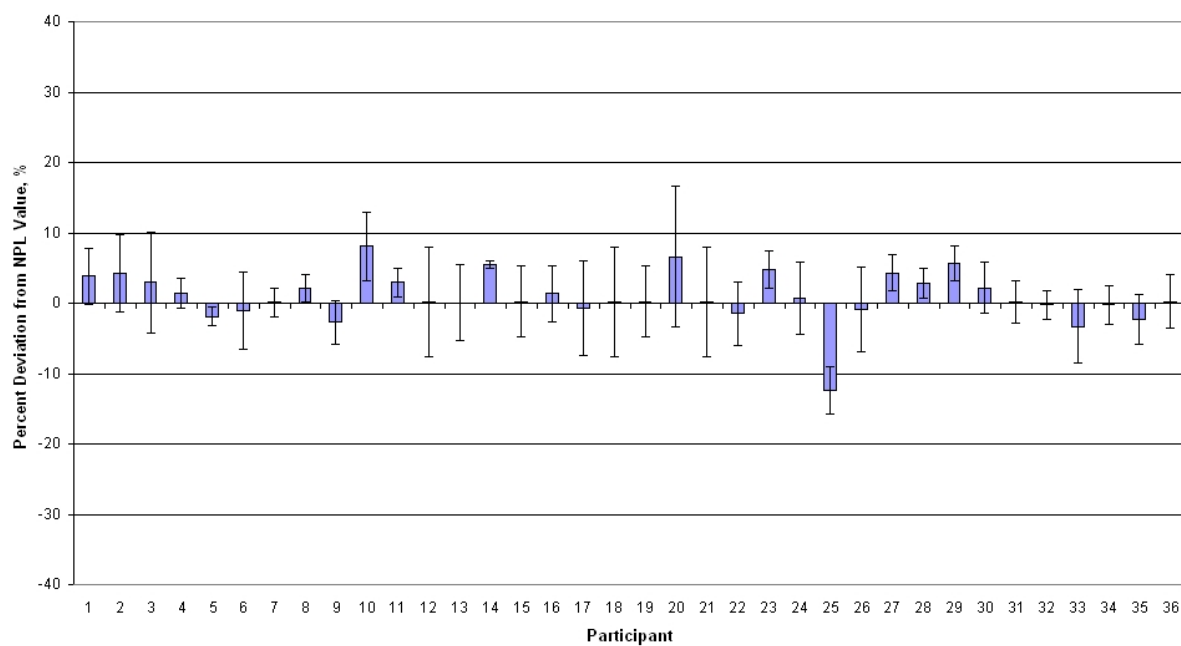


Figure 5
500 ppm NO percentage difference from assigned value and uncertainty error bars
attributed by participants

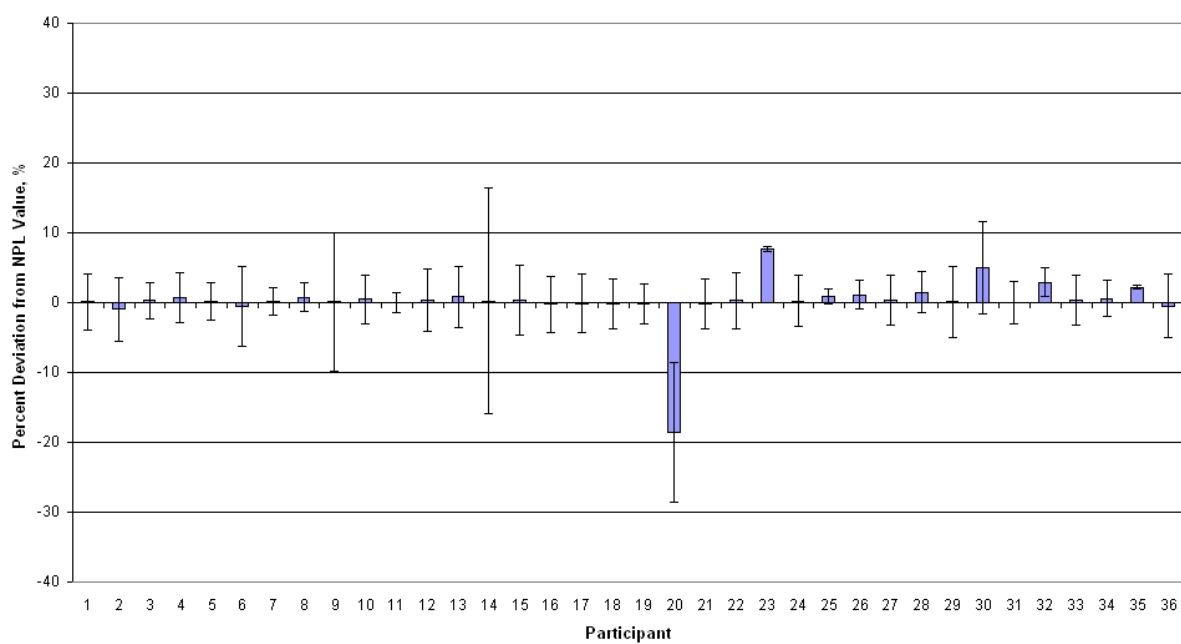


Figure 6
11 % O₂ percentage difference from assigned value and uncertainty error bars
attributed by participants

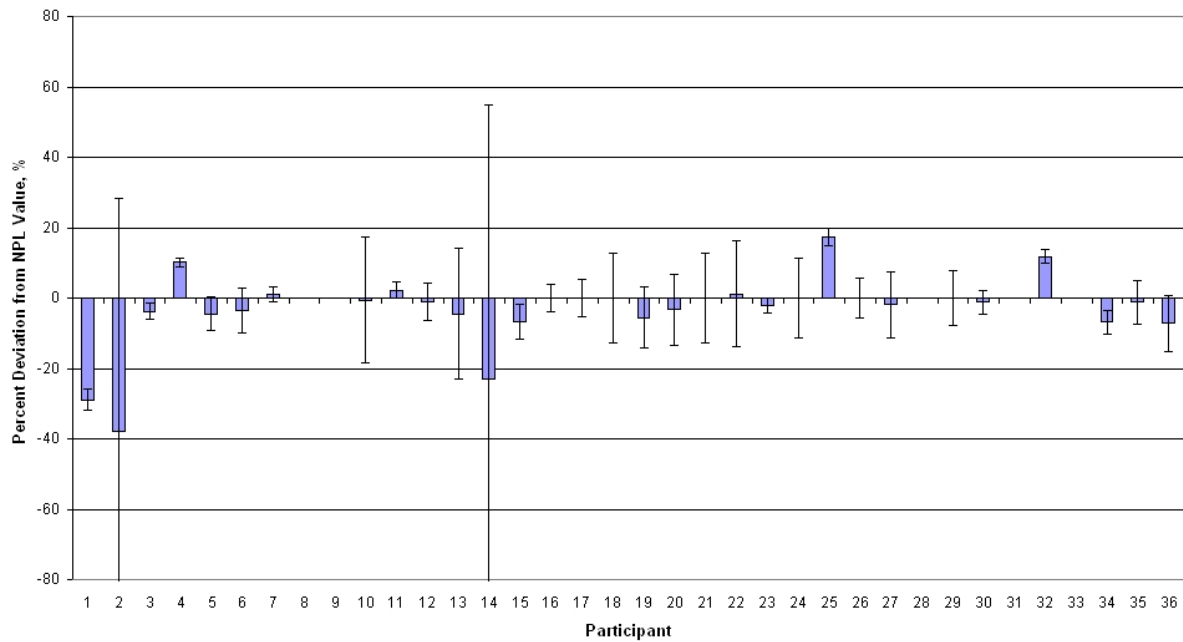


Figure 7
10 ppm C₃H₈ percentage difference from assigned value and uncertainty error bars attributed by participants

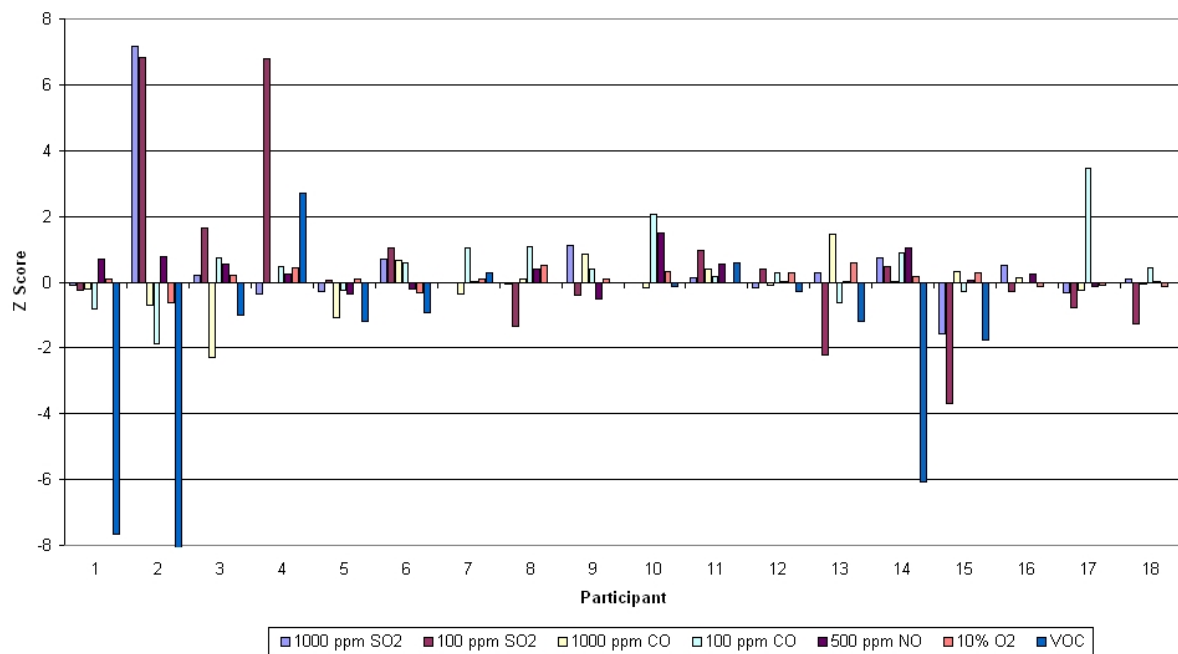


Figure 8
z scores for all species and participants 1 to 18

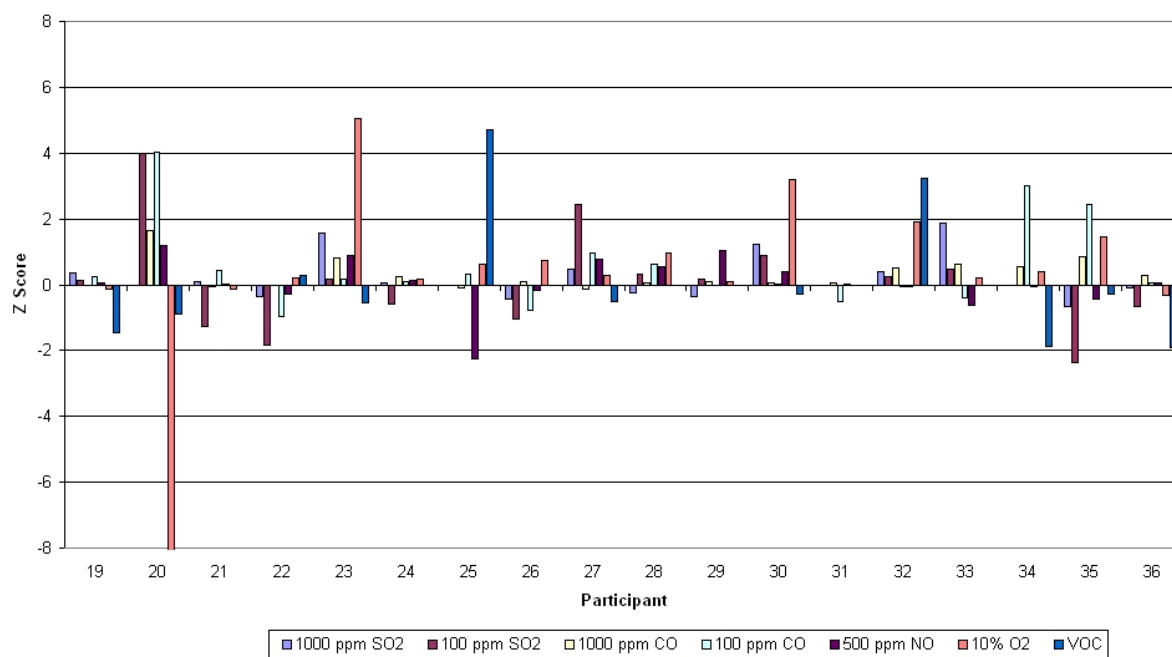


Figure 9
z scores for all species and participants 19 to 36

4 DISCUSSION

4.1 SO₂

Participants results showed good agreement with the assigned value. The average percentage deviation from the assigned value was 1.5% for the 1000ppm standard and 0.8% for the 100ppm standard.

4.2 CO

Participants results showed good agreement with the assigned value. The average percentage deviation from the assigned value was 0.4% for the 1000ppm standard and 1.6% for the 100ppm standard.

4.3 NO

Participants results showed excellent agreement with the assigned value. The average percentage deviation from the assigned value was 0.9%.

4.4 O₂

Participants results showed excellent agreement with the assigned value. The average percentage deviation from the assigned value was 0.2%.

4.5 C₃H₈

Participants results were most varied with the propane standard. The average percentage deviation from the assigned value was -3.2%.

4.6 UNCERTAINTIES

The uncertainties reported for the measurements of the standards were in general realistic with the majority of participant's uncertainties overlapping the assigned value. The variation however between reported uncertainties was large. Participants whose uncertainties are much larger than the deviation from the assigned value might investigate how they could tighten their uncertainty budgets increasing confidence in their measurements. Those participants who obtained an acceptable z score but whose uncertainties do not overlap the assigned value maybe underestimating their uncertainties. These participants could consider re-evaluating their uncertainty budgets.

4.7 CYLINDER CHECK

All cylinders returned with gas remaining were re-measured at the end of the proficiency test. Cylinders returned empty could not be checked for drift; however comparison measurements from cylinders of the same species and concentration show no significant drift. The re-measured values of the cylinders showed no statistical difference from the initial assigned values, and the re-measured values would not results in any participant's z score changing status level.