

NPL REPORT AS 14

Gaseous Proficiency Testing Scheme for the STA, Round 3 Final report

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Quality of Life Division

ABSTRACT

The report presents the results of the third round of the Gaseous Proficiency Testing Scheme administered by the STA.

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Approved on behalf of Managing Director, NPL
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1. Introduction

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

The gaseous 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. 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. PT Scheme Description and Third Round Results

Thirty-six STA member companies took part in the third round of the scheme, which involved the round robin measurement of a number of traceable standard gas mixtures.

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.

Species	Nominal Concentration
SO ₂ in Nitrogen	955 ppm and 80 ppm
CO in Nitrogen	860 ppm and 97 ppm
NO in Nitrogen	468 ppm
O ₂ in Nitrogen	11 %
Propane	9 ppm

Table 1. Gases used in the second round of the PT scheme

Three sets of test gases were circulated to different participants, each with a known concentration, traceable to NPL primary gravimetric gas standards. The purity of each sample was also checked to ensure no potentially interfering substances were present in the cylinders.

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 most reported uncertainties. The cylinder concentrations were deliberately chosen to be slightly different from the nominal values.

The results of each analysis were expressed as percentage differences from the true value. This allows a comparison to be made between the different gas samples used at each nominal concentration. 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. Overall the results are encouraging, with most participants reporting results within 10% of the true value.

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. One disadvantage of this approach is that the percentage deviation will depend on the species being measured; for example analysis of 1000 ppm CO might be expected to give better uncertainty than analysis of 500 ppm NO (This is reflected, for example, in the uncertainty requirements in the Waste Incineration Directive). Using this technique it is difficult to compare results from the analysis of different gases within a PT scheme.

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:

$ 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 the second round of the PT Scheme is the standard deviation of the results reported by the first round of the PT scheme. Therefore a z score of 2 or greater shows significant bias in the measured result and not random noise. Figure 2 summarises the z scores calculated in this way, and the results are given in Table 3. It can be seen that most results fall into the acceptable category, with only a few analyses falling into the unacceptable category.

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.

Participant	SO ₂		CO		NO	Oxygen	Propane
Code	1000 PPM	100 PPM	950 PPM	85 PPM	450 PPM	11%	9 PPM
A			-7.72	-20.01	1.04	1.37	
B	11.27	6.83		-0.67	0.20	-0.09	38.04
C	-8.38	0.50	-11.43	-2.37	37.21	-0.55	7.71
D	-1.83	-0.50	-2.15	-0.99	-4.41	-0.45	-0.88
E	16.99	7.05	0.65	-1.82	6.38	0.36	9.03
F		1.12		-4.63	-2.15	-2.28	-8.16
G	4.01	1.86	0.83		-0.23	1.01	14.13
H	1.05	-0.12	4.47	-1.55	0.83	-4.11	-17.23
I	0.63	-2.62	3.77	-1.55	0.41	-3.20	-17.23
J	-0.83	-1.86	0.36	-3.74	-1.09	0.37	
K			4.62	-0.47	-2.47	-0.63	-4.19
L	3.01	1.89	0.76	-0.47	-0.32	-2.44	-17.40
M	19.80	12.67	-1.03	1.28	-0.44	1.10	-5.43
N	0.27	-4.28	0.41	-6.20	0.11	-1.54	2.86
O	-1.04	3.11	-1.15	0.63	-4.09	-0.09	-4.35
P	0.22	-0.62	0.95	1.78	-0.23	-0.09	2.17
Q	-1.15	6.83	2.48	-0.10	11.03	-1.01	
R	2.60	-1.00	2.38	-1.04	3.38	0.27	3.17
S	3.32	23.60	0.99	-0.52	-2.15	0.82	13.38
T	3.53	-2.62	9.69	11.78	-1.08	3.20	13.38
U	0.33	-21.61	2.46	2.52	-2.59	1.74	-1.74
V	0.03	2.14	0.03	0.05	-0.40	-0.72	0.22
W	3.01	3.62	1.92	1.53	-4.91	-0.91	
X	0.33	0.62	0.16	-0.73	-1.51	-0.46	-0.23
Y	-1.25	-1.74	1.87		4.38	0.37	-0.76
Z	-0.94	5.59	-1.84	-2.71	0.63	0.82	
AA	-0.09	1.12	-0.91	-1.69	1.49	0.82	3.26
AB			-0.10	-0.94	-1.30	0.09	-7.61
AC	0.64	17.14	-1.15	-0.46	-0.23	0.18	-4.89
AD	0.85	0.99	-0.56	-2.20	-3.23	0.27	
AE	1.64	8.61	1.23	0.50	1.26	-0.64	
AF	1.11	1.12	1.58	-0.52	-0.02	0.82	
AG	2.48	-1.37	1.58	10.76	-4.27	-1.37	
AH	9.42	7.37	4.03	2.55	1.90	1.19	7.26
AI	-2.77	-6.37	0.65	-5.65	-6.83	-0.46	7.14
AJ	3.22	3.62	1.93	1.53	1.47	0.37	

Table 2. Percentage difference between reported results and NPL true value

Participant	SO2		CO		NO	Oxygen	Propane
Code	1000 PPM	100 PPM	950 PPM	85 PPM	450 PPM	11%	9 PPM
A			2.07	6.73	0.21	0.88	
B	2.90	2.04		0.22	0.04	0.06	10.29
C	2.19	0.15	3.07	0.80	7.32	0.35	2.00
D	0.47	0.15	0.57	0.33	0.86	0.29	0.24
E	4.38	2.07	0.17	0.60	1.24	0.24	2.41
F		0.33		1.56	0.42	1.47	2.12
G	1.03	0.56	0.22		0.04	0.65	3.82
H	0.27	0.04	1.20	0.52	0.16	2.65	4.47
I	0.17	0.78	1.01	0.52	0.08	2.06	4.47
J	0.21	0.56	0.10	1.26	0.21	0.24	
K			1.23	0.16	0.48	0.41	1.12
L	0.78	0.56	0.20	0.16	0.06	1.59	4.65
M	5.10	3.78	0.28	0.43	0.09	0.71	1.47
N	0.07	1.26	0.11	2.05	0.02	1.00	0.76
O	0.27	0.93	0.31	0.21	0.80	0.06	1.18
P	0.06	0.19	0.25	0.59	0.04	0.06	0.59
Q	0.30	2.04	0.66	0.03	2.15	0.65	
R	0.68	0.30	0.64	0.35	0.67	0.18	0.82
S	0.87	7.00	0.27	0.18	0.42	0.53	3.47
T	0.92	0.78	2.60	3.96	0.21	2.06	3.47
U	0.08	6.44	0.66	0.83	0.51	1.12	0.47
V	0.01	0.63	0.01	0.02	0.08	0.47	0.06
W	0.79	1.07	0.51	0.51	0.97	0.59	
X	0.08	0.19	0.04	0.24	0.30	0.29	0.06
Y	0.32	0.52	0.50		0.85	0.24	0.21
Z	0.24	1.67	0.49	0.91	0.12	0.53	
AA	0.02	0.33	0.24	0.57	0.29	0.53	0.88
AB			0.03	0.31	0.25	0.06	2.06
AC	0.17	5.11	0.31	0.16	0.04	0.12	1.32
AD	0.22	0.30	0.15	0.74	0.63	0.18	
AE	0.42	2.56	0.33	0.17	0.25	0.41	
AF	0.29	0.33	0.42	0.18	0.00	0.53	
AG	0.64	0.41	0.42	3.62	0.84	0.88	
AH	2.43	2.19	1.08	0.86	0.37	0.76	1.88
AI	0.72	1.89	0.17	1.90	1.34	0.29	1.85
AJ	0.83	1.07	0.52	0.51	0.29	0.24	

Table 3. z Scores

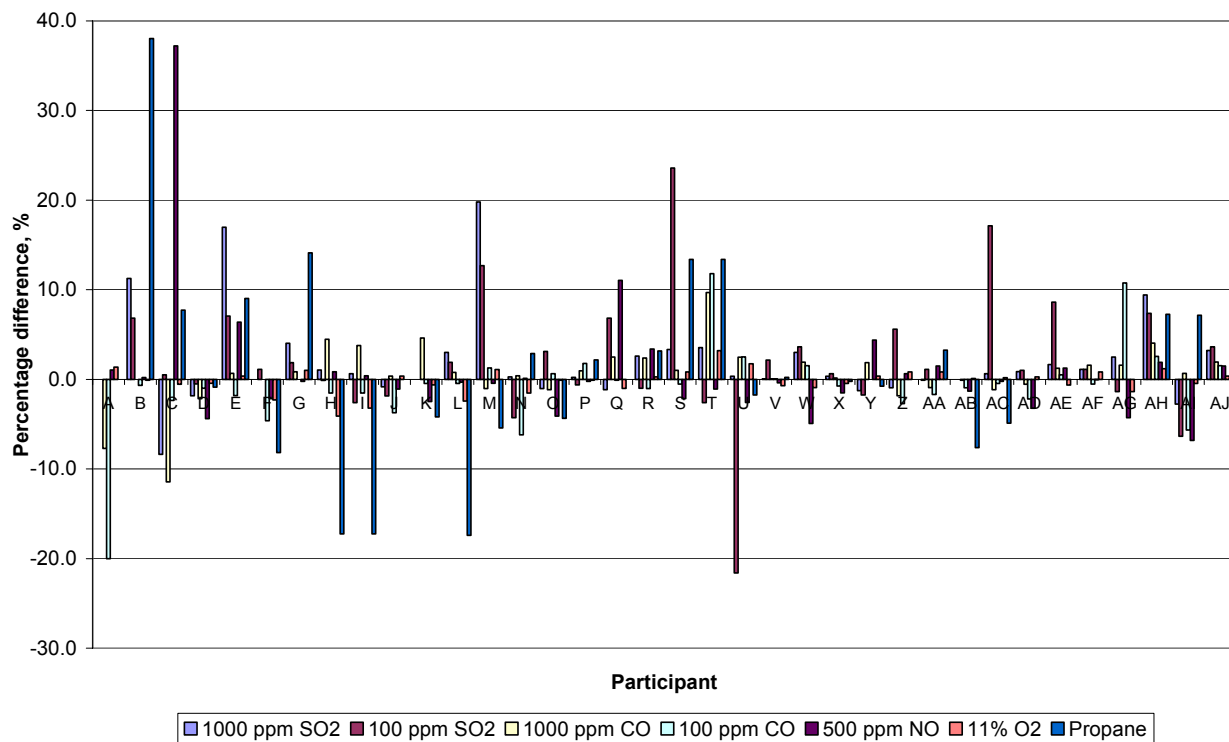


Figure 1. Percentage Difference from True Value

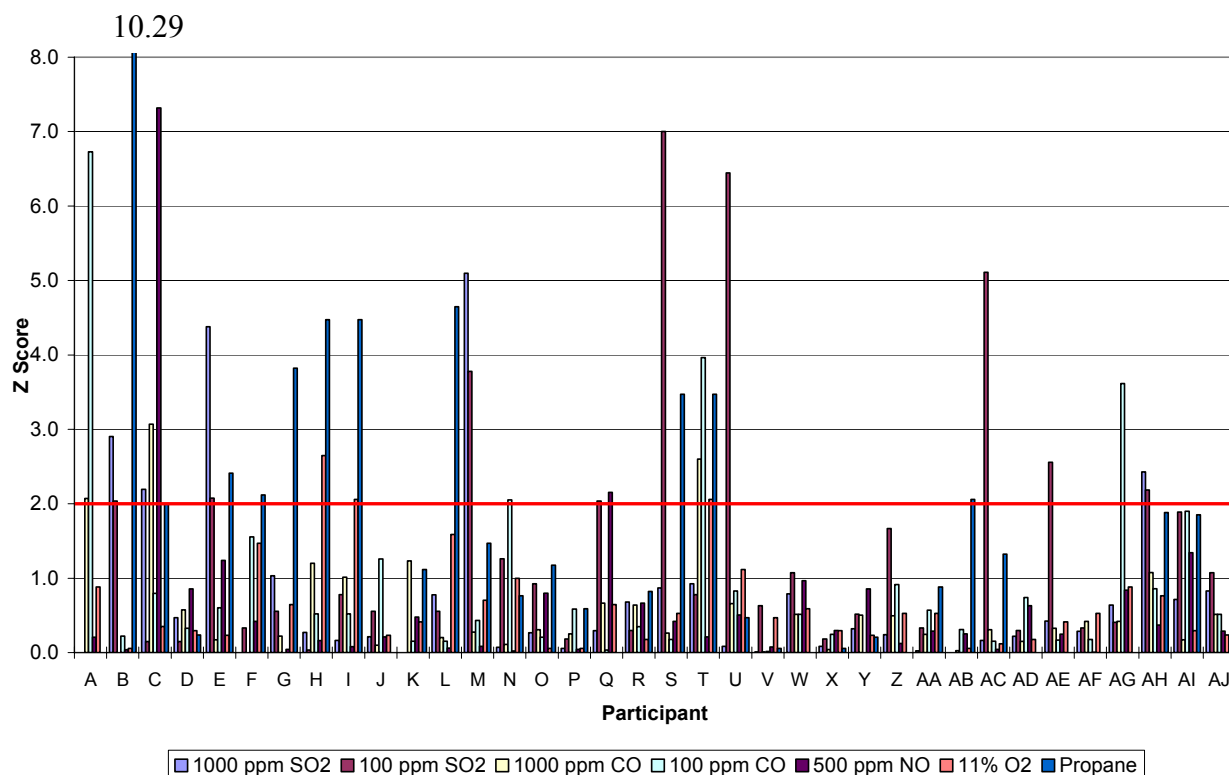


Figure 2. z Score

When the z Scores from the third round are compared with the z Scores from the second and first rounds, Figures 3 and 4, it can be seen that there has been a great improvement in performance by the participants between the first and second rounds and a slight improvement between the second and third rounds. The participant letters in the 1st, 2nd and 3rd rounds are not the same.

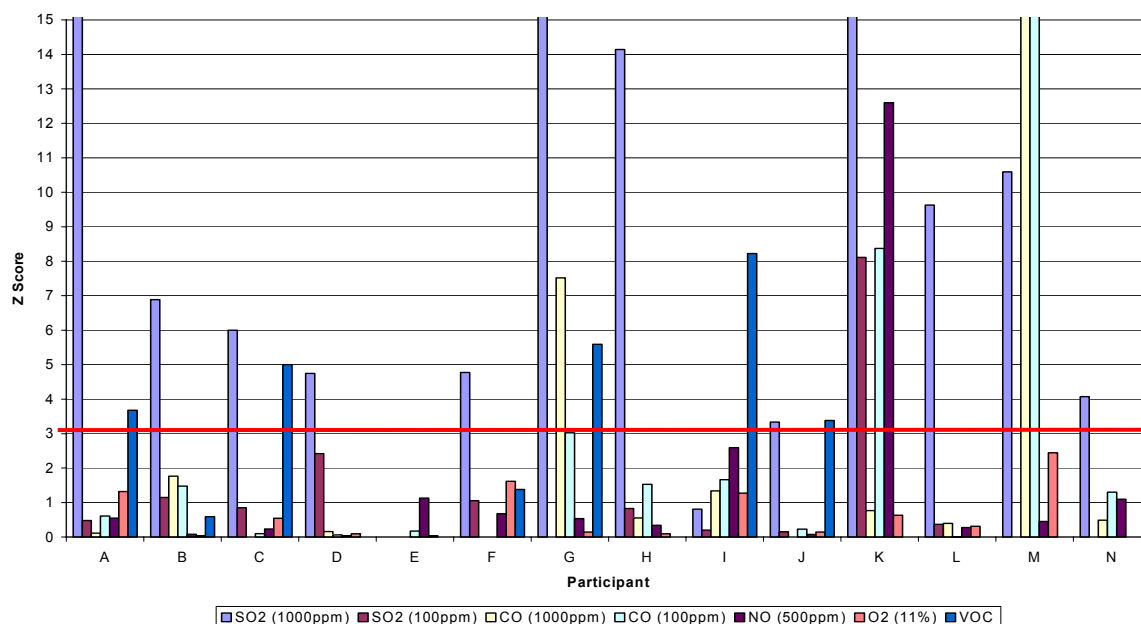


Figure 3. z Scores from the 1st round of the PT Scheme

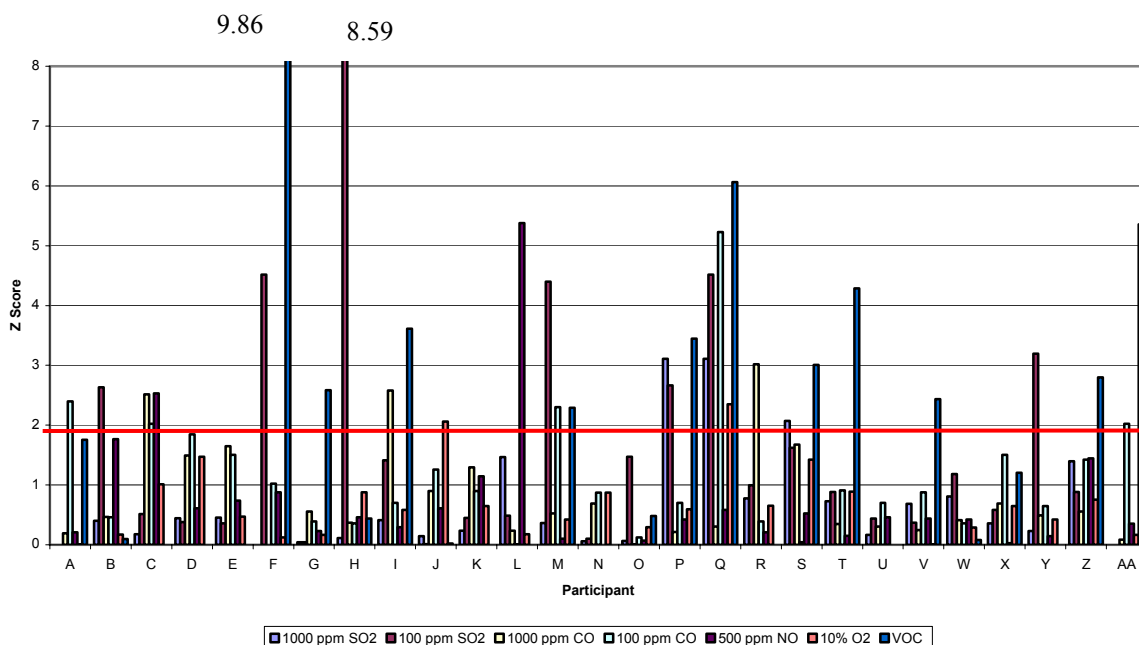


Figure 4. z Scores from the 2nd round of the PT Scheme

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Schedule

The following table show the dates the participants carried out measurements.

Note: Where dates were not recorded on the results sheet, the dates quoted are the dates when the results were submitted.

Lab	Date
A	05/12/05
B	12/12/05
C	06/01/06
D	19/01/06
E	05/01/06
F	26/01/06
G	20/02/06
H	23/02/06
I	23/02/06
J	26/01/06
K	20/02/06
L	17/03/06
M	10/04/06
N	06/06/06
O	30/05/06
P	04/07/06
Q	03/07/06
R	15/05/06
S	01/06/06
T	01/06/06
U	06/10/06
V	07/06/06
W	07/04/06
X	27/11/06
Y	20/04/06
Z	06/08/06
AA	05/12/06
AB	07/12/06
AC	04/01/07
AD	04/01/07
AE	19/05/07
AF	13/04/07
AG	03/07/07
AH	10/07/07
AI	16/03/07
AJ	28/08/07