NPL
National Physical Laboratory

REPORT

NPL REPORT AS 47

Gas measurement proficiency testing scheme, Round 1 Final Report

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NOT RESTRICTED

JANUARY 2010

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ABSTRACT

This report presents the results of the first round of the gas measurement proficiency testing scheme operated by NPL which was completed in April 2009.

ISSN: 1754-2928

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by

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1. INTRODUCTION

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

The gas measurement proficiency testing (PT) scheme provides a way of assessing the performance of laboratories by a series of regular inter-laboratory comparisons. The scheme was conducted at the stack simulator facility located at the National Physical Laboratory. The 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

Eight Source Testing Association (STA) member companies took part in the first round of the scheme, which involved measurement of combustion gases in five test conditions.

The PT scheme assessed the measurement of five test gases (NO_x, SO_2, CO, O_2 and VOC) at five simulated stack conditions. For each test, each sample gas has a known assigned value, determined by NPL. Up to four test teams operated on the stack simulator at one time and assigned values are specific to the day tested.

To determine the NO_x, SO_2, CO and O_2 assigned values a Horiba PG250 (with PS200) was run from a Baldwin Testerschoice gas conditioner. For VOCs a Sick Maihak FID was used. Both instruments use the standard reference methods (SRM) except for SO_2. However for SO_2 the Horiba PG250 (with PS200) has been proven equivalent to the SRM (NPL Report AS 26 – Validation of an Alternative Method for the measurement of SO_2 emissions using instrumental methods[1]).

Based on a theoretical dilution in the stack simulator the nominal concentrations for each test are shown in table 1.

Test	NO_x (ppm)	SO_2 (ppm)	CO (ppm)	VOC (ppm)	O_2 (%)	H_2O (%)
1	280	400	100	10	12	10
2	28	40	50	5	12	10
3	140	200	10	1	8	10
4	14	20	5	0.5	6	10
5	0	0	0	0	12	10

Table 1. Stack simulator nominal test concentrations.

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.

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

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 for σ in the calculation of the z score was derived with reference to LCPD, WID and the Environment Agency's M21 (SO_2 Instrumental Method). These provide requirements on allowable uncertainties of the measurement of NO_x, SO_2, CO and VOCs as a percentage of an ELV. The relevant CEN standard methods also give guidance on the allowable uncertainties as a percentage of emission limit values (ELV's). A nominal ELV for the stack simulator was selected for the calculation of the required sigma. The same ELV was used for all measurements of a given measurand (as otherwise target uncertainties at the lower concentrations would become unrealistically demanding).

	Uncertainty requirement (95% expanded)	Sigma (% of measured)	Nominal ELV	Target sigma
SO_2	10	5	400 ppm	20 ppm
CO	6	3	100 ppm	3 ppm
NO_x	10	5	300 ppm	15 ppm
VOC	15	7.5	50 ppm	3.75 ppm
O_2	6	3	15 %	0.45 %vol

Table 2. Value of sigma

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. DESCRIPTION OF STACK SIMULATOR TEST FACILITY

The NPL stack simulator is able to reproduce a wide range of simulated stack gases under controlled conditions. The simulator is a recirculating system, which recreates a cross section of a 1.5 m duct. Four standard 5 inch ports are available for sampling probes or cross stack instruments to be installed. In addition a number of extractive gas analysers may be connected to gas extraction ports. Figure 1 shows a schematic of the stack simulator.

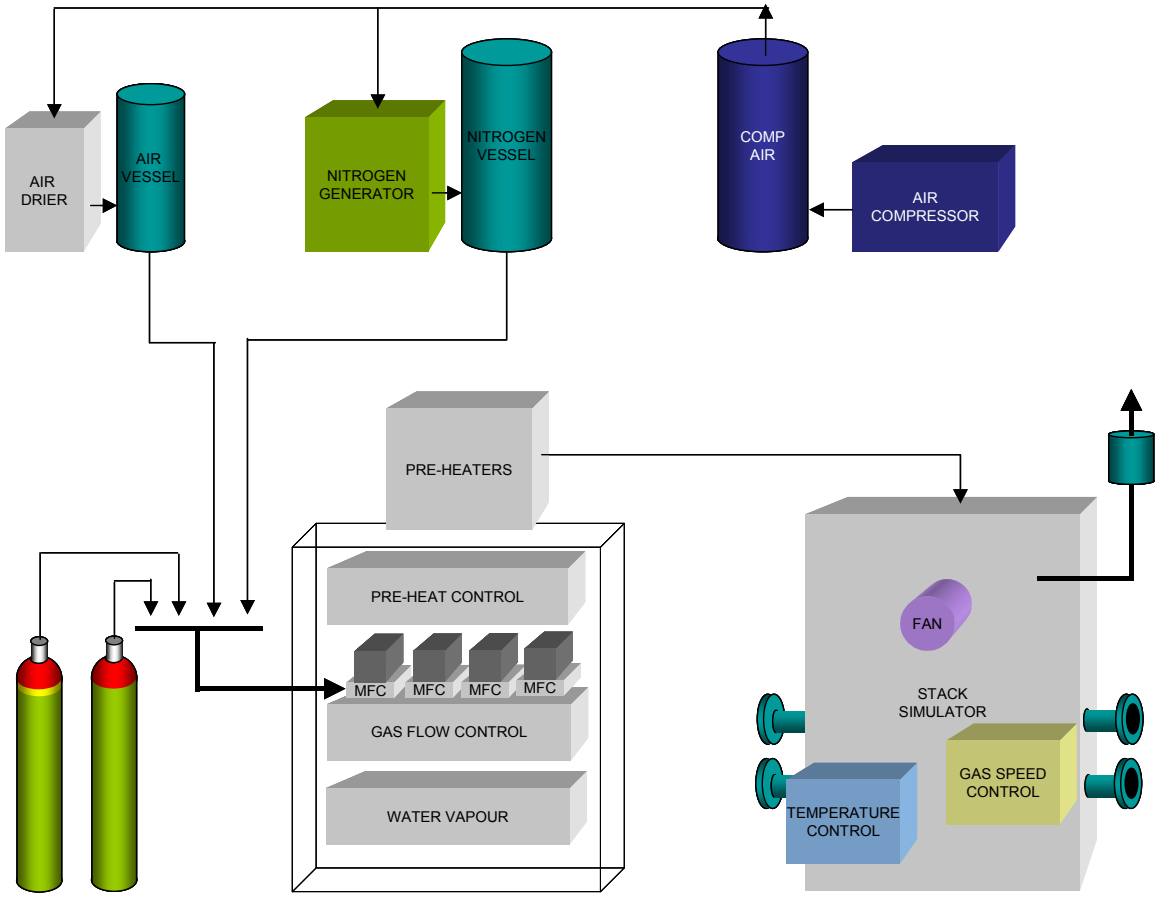

Figure 1. Schematic of outline of stack simulator

The stack simulator is able to generate the conditions in Table 3.

Performance Summary	
Temperature	up to 180 °C controlled to ± 2 °C measured to ± 0.5 °C
Gas vertical velocity	up to 12 metres per second
Water vapour	up to 25% by volume
Oxygen content	up to 20% by volume
Input gas flow rate	up to 300 litres per minute

Table 3. Range of stack conditions achievable in the NPL Stack Simulator.

The stack simulator is able to generate a mixture of test gases by blending test gases from cylinders with nitrogen and zero air from reservoirs. The bulk gas delivery is controlled by two 150 l/min mass flow controllers, allowing a blend of nitrogen and zero air. This enables reduced oxygen concentrations to be generated, simulating combustion gas conditions. Two further mass flow controllers allow the introduction of test gases, typically these consist of gas mixtures representative of combustion or waste incineration processes, i.e. SO_2 CO, NO_x. Complex gas mixtures are generated by using source gas cylinders containing a mixture of gases. The stack simulator has two low flow (~1 l/min) mass flow controllers in usual operation, though additional gas generation facilities can be added for more complex matrices.

The conditions within the sample region of the stack simulator have been previously verified to be well mixed in both axes. Figure 2 shows an example of the validation of the flow profile across the stack simulator test region.

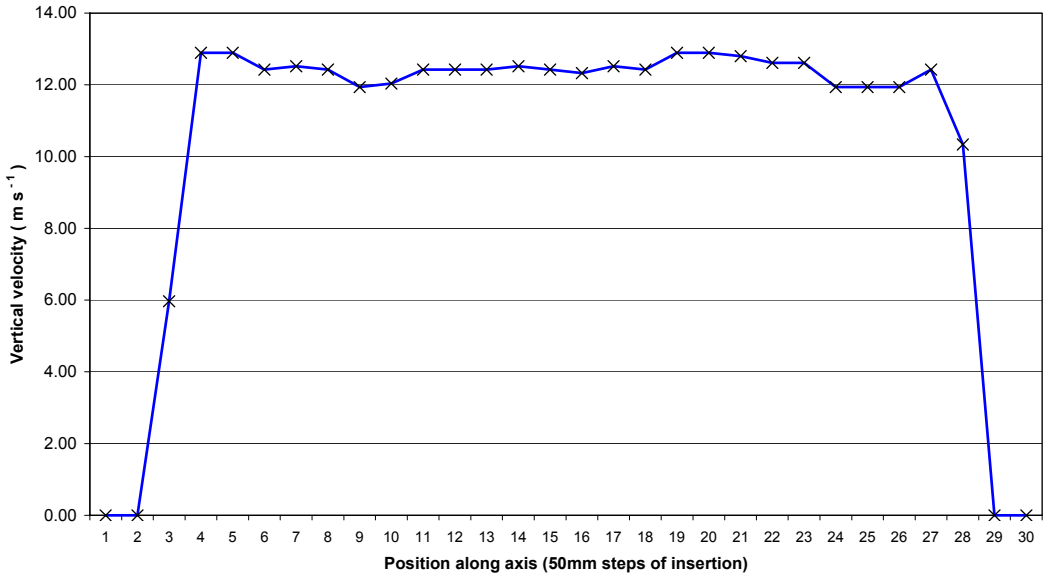

Figure 2. Plot showing flow stability across test region of stack simulator.

4. RESULTS

The following tables and charts illustrate the results for each participant. Tables 4, 5 and 6 give the assigned values and expanded uncertainties (95% confidence; k=2) for each test against which participants were compared.

Test	SO_2 (ppm)	SO_2 uncertainty (ppm)	CO (ppm)	CO uncertainty (ppm)	NO_x (ppm)	NO_x uncertainty (ppm)	VOC (ppm)	VOC uncertainty (ppm)	O_2 (%)	O2 uncertainty (%)
1	370.2	17.2	96.2	2.6	263.1	12.9	10.7	2.0	12.3	0.4
2	33.2	2.5	48.9	1.8	25.0	1.5	5.2	2.0	12.4	0.4
3	180.7	8.6	11.6	1.4	131.5	6.5	1.9	2.0	9.4	0.3
4	13.6	2.1	6.9	1.4	11.9	1.1	1.5	2.0	7.7	0.3
5	0.0	2.1	0.0	1.4	0.0	0.9	0.9	2.0	12.5	0.4

Table 4. Assigned values and their uncertainties from 21st April 2009

Test	SO_2 (ppm)	SO_2 uncertainty (ppm)	CO (ppm)	CO uncertainty (ppm)	NO_x (ppm)	NO_x uncertainty (ppm)	VOC (ppm)	VOC uncertainty (ppm)	O_2 (%)	O2 uncertainty (%)
1	367.5	17.1	96.0	2.6	258.5	12.7	9.2	2.0	12.3	0.4
2	36.0	2.4	48.7	1.8	25.8	1.5	5.1	2.0	12.4	0.4
3	184.6	8.7	11.3	1.4	133.8	6.6	1.9	2.0	9.5	0.4
4	15.6	1.7	6.6	1.4	11.9	1.1	1.5	2.0	7.4	0.3
5	0.0	1.5	0.0	1.4	0.0	0.9	0.9	2.0	12.4	0.4

Table 5. Assigned values and their uncertainties from 22nd April 2009

Test	SO_2 (ppm)	SO_2 uncertainty (ppm)	CO (ppm)	CO uncertainty (ppm)	NO_x (ppm)	NO_x uncertainty (ppm)	VOC (ppm)	VOC uncertainty (ppm)	O_2 (%)	O2 uncertainty (%)
1	371.2	17.3	98.2	2.7	248.1	12.1	9.6	2.0	12.2	0.4
2	36.1	2.6	49.6	1.8	23.7	1.5	5.3	2.0	12.4	0.4
3	179.7	8.5	10.9	1.4	122.5	6.0	1.9	2.0	9.6	0.4
4	16.1	2.2	6.2	1.4	10.9	1.0	1.5	2.0	8.1	0.3
5	0.0	2.0	0.0	1.4	0.0	0.9	0.9	2.0	12.5	0.4

Table 6. Assigned values and their uncertainties from 23rd April 2009

Figures 3, 5, 7, 9 and 11 give the z scores for each measurand grouped by test number. Figures 4, 6, 8, 10 and 12 give the ppm difference from the assigned value plus reported uncertainty bars grouped by participant.

During the tests there were technical problems with Participant I's sampling equipment, which lead to their drift during each test being greater than that allowed. Therefore, no measurement uncertainty can be attributed to their results and their reported concentrations treated with caution. The problems were bad enough during Test 2 for their results not to be reported for this test.

The gaps in results for some measurands are a result of participants choosing not to participate.

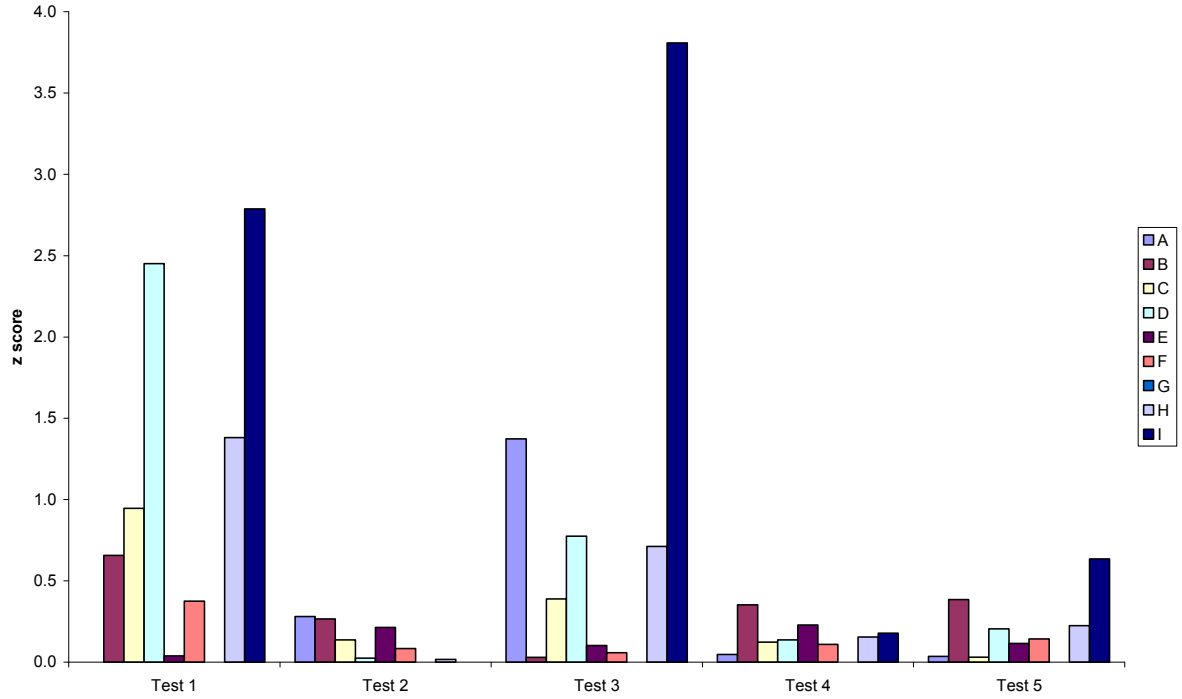

Figure 3. SO_2 z scores

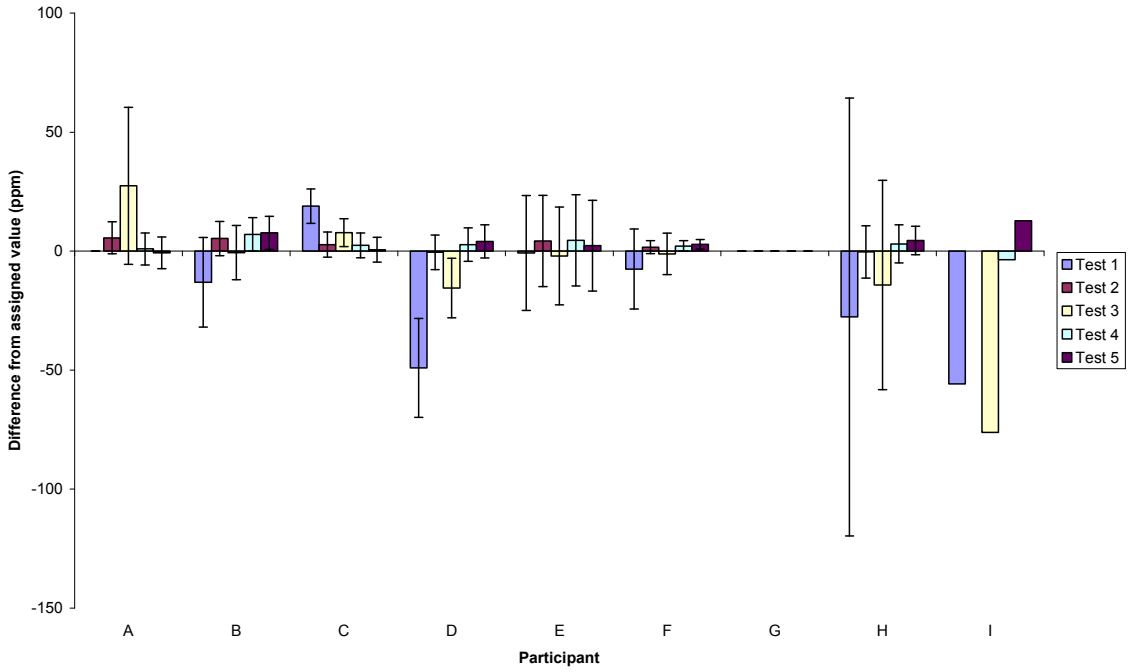

Figure 4. SO_2 ppm difference from assigned value with uncertainty bars

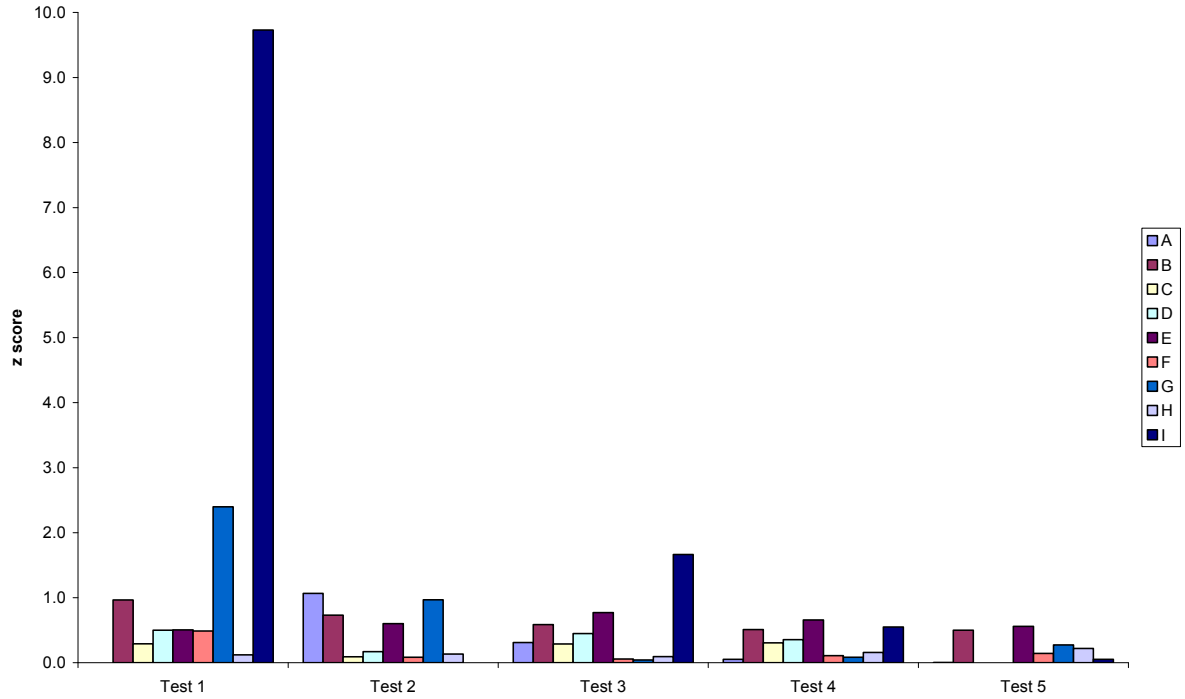

Figure 5. CO z scores

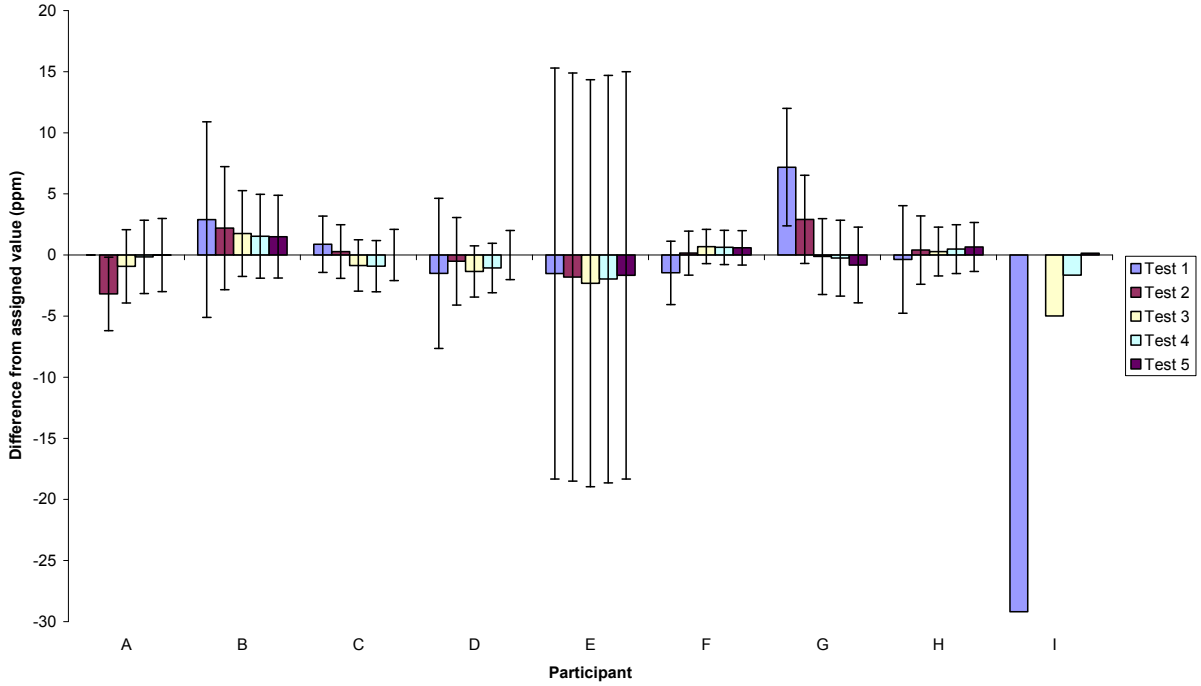

Figure 6. CO ppm difference from assigned value with uncertainty bars

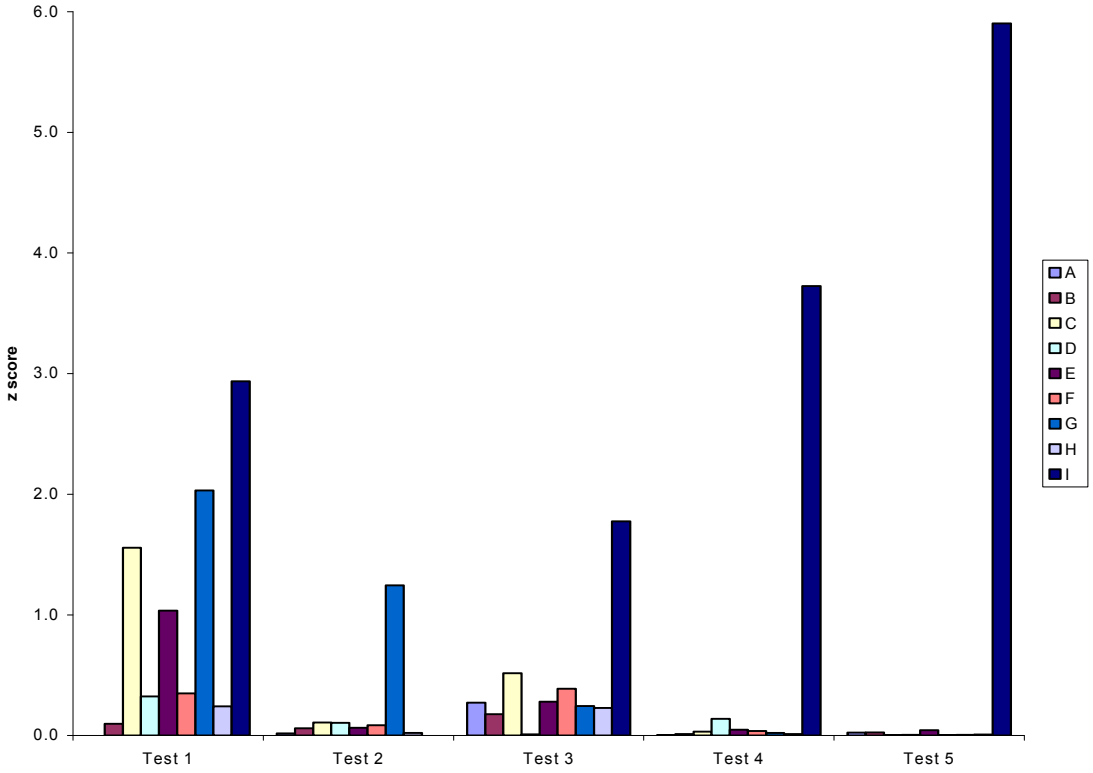

Figure 7. NO_x z scores

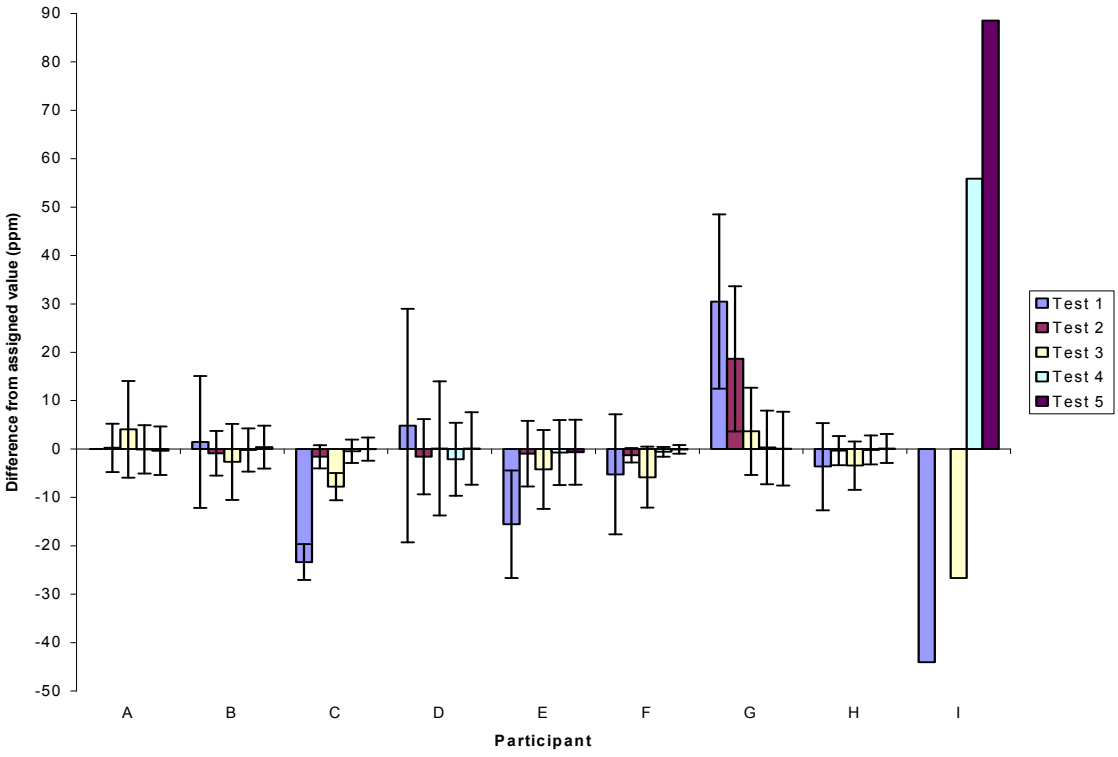

Figure 8. NO_x ppm difference from assigned value with uncertainty bars

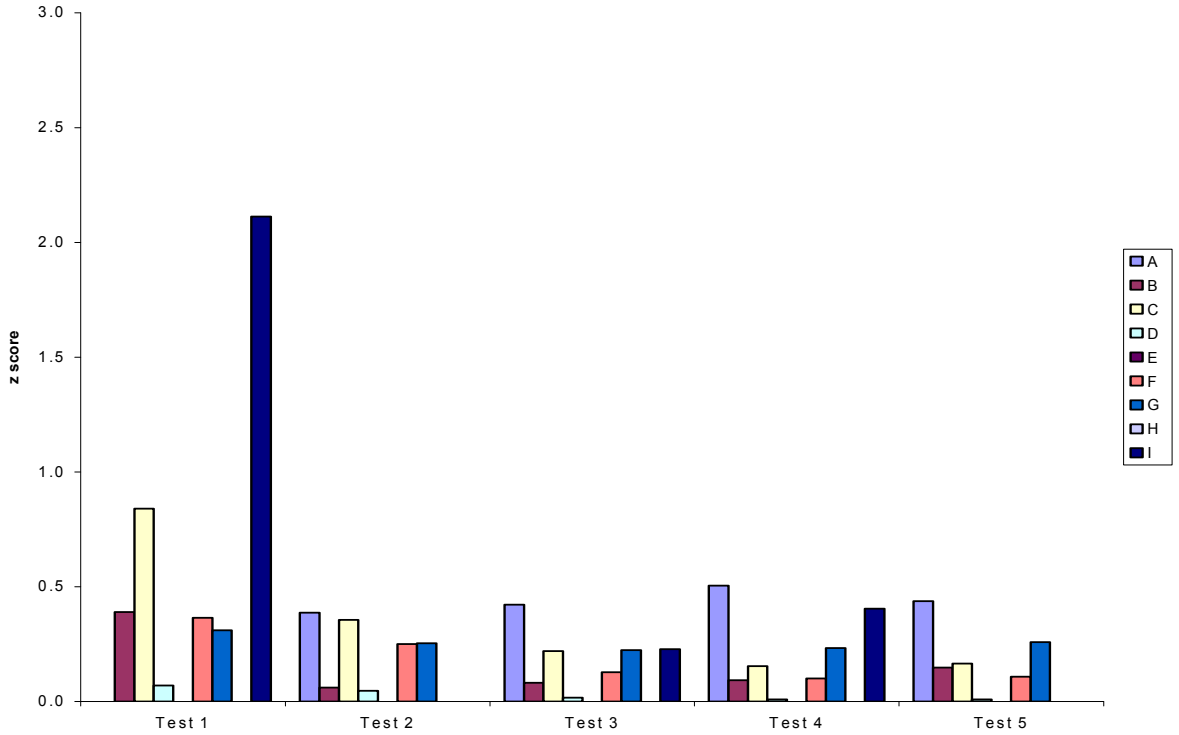

Figure 9. VOC z scores

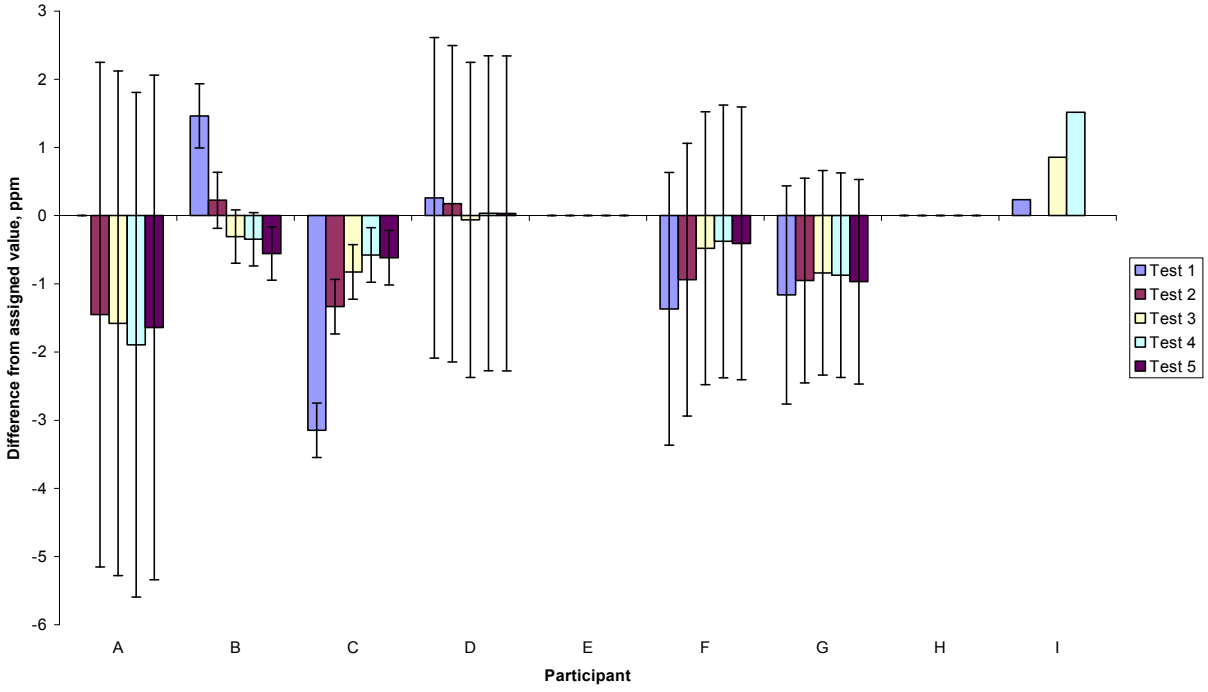

Figure 10. VOC ppm difference from assigned value with uncertainty bars

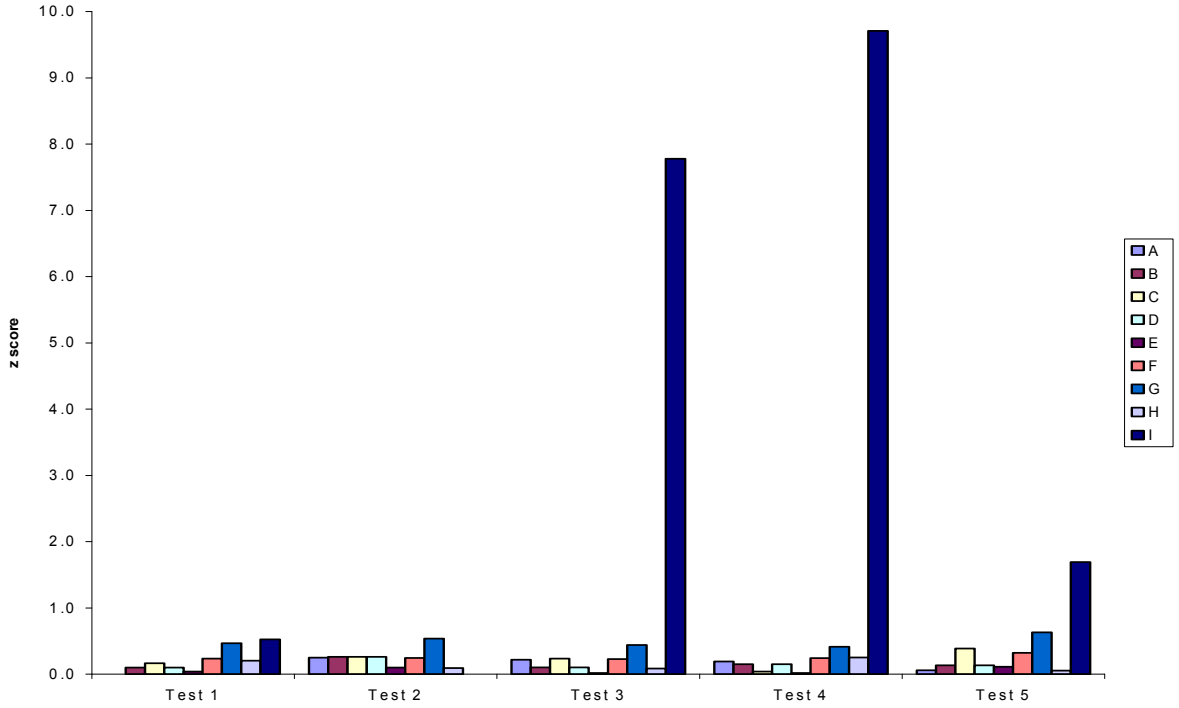

Figure 11. O_2 z scores

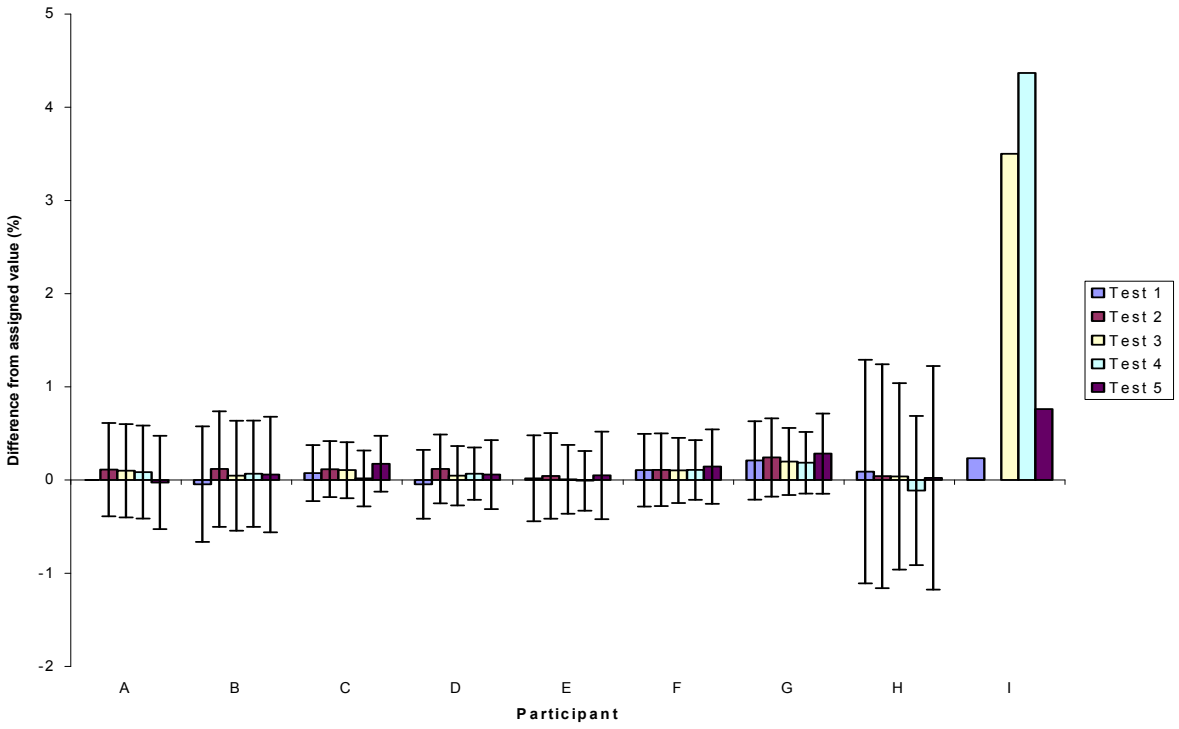

Figure 12. O_2 absolute % difference from assigned value with uncertainty bars

5. CONCLUSIONS

Participant I's results are not included in the conclusions due to their measurement problems and lack of reportable measurement uncertainty.

Overall the performance of participants was excellent with only two participants outside the acceptable range for NO_x and CO. These exceedences only occurred at the high concentration test one. There was also a general trend of lower z scores at the lower concentrations however the performance requirements were the same at the high and low range tests so this would be expected.

The results of the participants show no bias for NO_x, SO_2 and CO with the number of participants under or over reading being evenly distributed. Oxygen was consistently over read by 0.1% to 0.2% across all five tests indicating a systematic error either in the assigned value or participant's results. It is unlikely that each participant had a similar leak in their sampling system as this would show up in participants under reading the other measurand. The most likely explanation is a fault in calibration either of the reference instrument for O_2. However a difference of this magnitude is insignificant when compared to the achievable uncertainty using a Horiba PG250.

A similar systematic error was seen in four out of six participant's results for VOCs. However we have to consider the measurement range and uncertainty of the FID in use. A 1 to 2% difference relative to the measurement range is within the detection limit and allowable uncertainty of the analyzer as stated by BS EN 12619:1999.

6. ACKNOWLEDGEMENTS.

The authors of this report would like to acknowledge the support from the STA in administration of the scheme.

7. REFERENCES

1. NPL Report AS 26 – Validation of an Alternative Method for the measurement of SO_2 emissions using instrumental methods. Rod Robinson, Marc Coleman, Matthew Williams, Robert Elliott, Martin Clack and Andrew Curtis.