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GAS STANDARDS RELEVANT TO STACK EMISSION MEASUREMENTS AT THE NATIONAL PHYSICAL LABORATORY

PE Holland, PT Woods, RH Partridge, RA Robinson and MJT Milton

Environmental Standards Section
Centre for Optical and Environmental Metrology
National Physical Laboratory
Teddington TW11 0LW, UK
Tel: 0181 943 7174 Fax: 0181 943 6755 e-mail: Paul.Holland@npl.co.uk

1. INTRODUCTION

NPL is one of a number of laboratories which forms part of the Governments policy to ensure that UK measurements of all kinds are accurately made through the DTI's National Measurement System. NPL is the focus of the United Kingdom's physical measurements and its remit includes aspects of environmental measurements, which form an important component of the UK's Valid Analytical Measurement (VAM) programme.

Atmospheric pollution, arising from sources such as motor vehicles, aircraft and industrial and electrical plants, is of growing concern throughout the world. As a result, new and progressively more stringent legislation is being introduced to control its impact on the environment. Successful implementation of such legislation requires instruments that measure pollution levels traceably and accurately.

Examples include measurements of:

- exhaust emissions from automobile and aircraft engines;
- emissions from chemical and combustion processes;
- air quality in rural and urban areas and work place atmospheres.

Traceability is generally achieved in such measurements by utilizing one or more reference gas mixtures to calibrate the monitoring instruments. The reference mixtures are themselves traceable to accurate primary gas standards produced by national standards laboratories or similar organisations.

The National Physical Laboratory (NPL) produces and maintains primary gas standards of a range of gas mixtures relevant to stack measurements. These standards, which are prepared by absolute gravimetric methods, are used to certify gas mixtures, known as secondary gas standards. These secondary gas standards are subsequently employed as working standards by UK industry and government laboratories.

This paper provides a short description of the NPL primary gas standards facility, discusses the methods used to prepare and certify a range of primary and secondary gas standards and gives the uncertainties assigned to the concentration values of these secondary standards.

Some of these secondary standards have been used as part of a proficiency testing programme within the STA. Eighteen participants were involved in a ‘round robin’ exercise measuring three gases (carbon monoxide, nitric oxide and sulphur dioxide) at emission levels. The results of this pilot proficiency testing programme will be presented.

2. THE NPL PRIMARY GRAVIMETRIC FACILITY

Primary gas standards are prepared at the NPL in passivated aluminium-alloy cylinders using an absolute gravimetric process. The parent gases employed for this process have their purities comprehensively verified using different analytical techniques. The concentrations of these prepared standards are subsequently validated using stringent accuracy and stability tests. An outline of these is given below.

2.1 PREPARATION PROCEDURE

2.1.1 Purity Analysis of Components

The gaseous components used in the preparation of gas standards are rigorously analysed before use with the following dedicated instrumentation.

(i) A high resolution, rapid scanning, fourier-transform spectrophotometer coupled to a multi-pass absorption gas cell which can be operated with path lengths between 4 and 120 metres. This facility identifies and measures quantitatively any gaseous species present which has an infrared absorption spectrum in the wavelength range 600 to 4000 cm^{-1} as this covers the strong absorption bands of virtually all infrared-active gases. By comparing the amount of absorption from a gas of unknown concentration with that from a similar gas of known concentration the unknown concentration can be determined.

(ii) Gas chromatography involves passing the test gas through a column coated with a suitable Stationary phase. Components in a mixture have different tendencies to adsorb onto the column surface or dissolve in the purge gas and will hence traverse the column at different rates. The components will emerge from the column at different times after the test gas was first injected. Suitable detectors are then used to compare the peak area from the standard mixture against the unknown, thus determining the unknown concentrations

2.1.2 Instrumentation for Preparing Gas Standards

All primary and secondary gas standards are prepared gravimetrically in aluminium-alloy cylinders. These cylinders are currently obtained from BOC Ltd, Scott and Air Products and are passivated using their proprietary processes. Tests carried out at NIST (National Institute of Standards and Technology USA), NPL and elsewhere have shown the concentrations of most gas mixtures stored in these types of cylinders remains stable in excess of two years, and in many cases for more than five years.

NPL have shown certain gases to be more stable in cylinders which have undergone specific passivation processes, thus a specific cylinder treatment can be chosen for a particular requirement. Over the past years NPL has worked closely with cylinder manufacturers to improve these passivation techniques and increase the stability of non-reactive gases (CO, CO_2, $C_3H_{8,}$, CH_4), and more recently reactive gases (NH_3, Cl_2 and HCl).

High vacuum evacuation apparatus is used to evacuate the passivated cylinders prior to filling. A computer controlled mass spectrometer is connected to the vacuum apparatus and is used daily for on-line diagnostics of impurities and leaks.

A gas blending system specially developed by NPL is used to transfer the pure parent gases and gas mixtures into the recipient cylinders. This method is used both in the preparation of primary and secondary gas standards. Calibrated pressure and on-line mass measuring instrumentation is used to indicate the gas mixing ratio and the final gas concentration is defined from the molar fraction determined from accurate mass measurements. These accurate mass measurements are performed using two pan equal arm bullion balances.

2.1.3 Gravimetric Preparation Process

Gas standards are generally first prepared by a ten to one dilution process from the nominally pure parent gases. These standards are then used as the sources of further dilutions.

The passivated cylinders used to contain the mixtures are initially evacuated for a period of at least 48 hours, or until a pressure of less than 10^{-2} Pa is achieved. Prior to the cylinder removal from the evacuation line, a mass spectrum is produced to check for residual concentrations of extraneous gaseous species which may contaminate the standard in production.

Each evacuated cylinder is weighed on a two pan balance against a tare cylinder of nominally identical volume. The cylinder is then attached to the filling line and the line is evacuated to less than 10^{-2} Pa. Approximately 10 bar of minor gas component is transferred into the cylinder, which is then re-weighed on the same two pan balance. The cylinder is then filled with a predetermined mass of nitrogen or synthetic air using the on-line weighing system. The cylinder is finally re-weighed and the masses of the minor and major components are calculated. These values are then used by the NPL software (Gravcalc) which calculates the absolute mole fraction and uncertainty of the new gas mixture. The mole fraction and uncertainty expressions can be seen below:

X_k is the gravimetric concentration for each of the components and is calculated by:

$$X_k = \frac{\sum_{j=1}^{P} \frac{(m_j.X_{jk})}{(\sum_{i=1}^{n} X_{ij}.M_i)}}{\sum_{j=1}^{P} \frac{m_j}{(\sum_{i=1}^{n} X_{ij}\ .M_i)}}$$

where:

P = number of parent gases
j = j^{th} parent gas
n = number of quantified components in final mixture
i = i^{th} component in cylinder j
k = k^{th} component in final mixture
M_i = relative molecular mass of component i
X_{ij} = mole fraction of component i in parent gas j
m_j = mass of j^{th} parent gas in the final mixture

and the uncertainty is calculated from the following expression:

$$U_c^2(X_k) = dX_k^2 = \left[\sum_{t=1}^{n}\left(\frac{\partial X_k}{\partial M_t}\right)^2 .\left(dM_t\right)^2 + \sum_{s=1}^{p}\left(\frac{\partial X_k}{\partial M_s}\right)^2 .\left(dM_s\right)^2 + \sum_{s=1}^{p}\sum_{t=1}^{n}\left(\frac{\partial X_k}{\partial X_{ts}}\right)^2 .\left(dX_{ts}\right)^2\right]$$

where:

dm_s = standard uncertainty in the weighed mass from cylinders
dM_t = standard uncertainty in the relative molar mass component t
dX_{ts} = standard uncertainty in the mole fraction of component t in cylinders

This expression relates to standard uncertainties which are not correlated and have a simple non linear functional form.

Standards with nominally the same value are prepared with similar concentrations (within 2% to 4% relative of value). After rigorous quality assurance measurements and analytical tests have been carried out to validate their concentrations and stability, the prepared standards are used as sources of subsequent dilutions. Using this method, a family of gas standards is produced from about 10% (mole/mole) to 1 ppm. Several independent families of standards are prepared for each type of gas mixture and these independent families are used as one aspect of the procedure for validating the accuracy of the complete range of standards.

2.1.4 Validation of Primary Gravimetric Standards

The procedure used to validate the absolute concentrations of the range of NPL gravimetric standards has several stages, as indicated below:

(i) The instruments and techniques outlined in Section 2.1.1 are used to check the concentration of all gaseous constituents in the standards other than the specified minor and major components.

This verifies that no impurities or extraneous species have become entrained into the cylinders during the preparation process and that no subsequent chemical reactions have taken place.

(ii) All the sources of uncertainty, both type A and B which occur during the complete preparation process are itemised and quantified. These are then combined in a square root sum of squares manner to produce a combined uncertainty, which is then used to produce an expanded uncertainty with the use of an appropriate K factor.

The value of this uncertainty will depend on a number of factors including the purity of the component gases, the weighing procedure and the uncertainties arising from the relative molar masses.

(iii) The primary standard is intercompared against two or more existing primary standards using an instrument with sufficient repeatability to demonstrate that their measured and gravimetric values are consistent within the overall uncertainties indicated in (ii) above. The intercomparison procedure involves using the primary standards with the smallest and largest concentrations to bracket the new primary standard which is treated as an unknown. If the analytical value obtained for the new standard differs significantly from its gravimetric value, (typically ± 0.3%) it indicates an inconsistency in the new standard and it is discarded. To date, no such discrepancies have been detected.

(iv) Standards with similar concentrations from different families are also intercompared using the procedure outlined in (iii). These measurements are carried out over the entire concentration range in order to demonstrate the consistency of the complete set of standards of a given component mixture.

(v) Repeated intercomparisons are carried out in the manner outlined in (iii) above to demonstrate the long-term stability of the set of standards.

(vi) New batches of standards are produced regularly. These are intercompared with each other and also with older standards using the procedure outlined in (iii) to confirm the accuracy of the overall process.

(vii) NPL's gas standards are regularly intercompared with those of other national standards laboratories. A comprehensive measurement exercise carried out with the National Institute of Standards and Technology (NIST) USA (1) demonstrated the consistency of the CO/N_2 and CO_2/N_2 standards prepared by NPL and NIST over a wide range of concentrations. A similar intercomparison exercise was also completed on the concentration range of NO/N_2, C_3H_8/air and C_8H_3/N_2 standards. Similar intercomparisons have also been carried out with the Netherlands MeetInstituut (NMi), The Netherlands as part of the Euromet agreement.

(viii) A series of 'round-robin' intercomparisons are organised by Comité (CIPM). These are carried out to investigate the international uniformity of gas standards produced by selected laboratories.

3. SECONDARY GAS STANDARDS

3.1 PREPARATION PROCEDURE

Secondary gas standards are prepared in-house using the parent gases of the same specifications as those employed for the production of the primary gravimetric standards. This ensures that the gases used are of certified purity and contain no species that would affect the certified concentration values or be detrimental to the stability of the mixtures. The purity of the parent gases are checked against the manufacturers specification using gas chromatography and fourier-transform infrared techniques.

The secondary gas standards are blended using the same apparatus as that employed to prepare the primary gravimetric standards. Precise measurements of the gas pressure and gas mass at each stage in the process enables the concentrations of the mixtures to be produced to within ± 1% of the concentration of the appropriate NPL gravimetric standard. Up to 3 mixtures with the same nominal concentrations can be produced together. The mixtures are subjected to stability checks before their concentrations are certified with respect to NPL primary standards.

3.2 CERTIFICATION PROCESS

The gravimetric secondary gas standards are checked soon after preparation to confirm that their concentrations are as expected. They are then allowed to stand for a defined period before final certification is carried out. Following this period, all secondary standards are certified individually against NPL's gravimetrically prepared primary gas standards.

3.2.1 Apparatus

The Automatic Gas Analysis System (AGAS) is used to certify the concentrations of secondary standards. The AGAS has dedicated gas analysers for each of the species used in the standards. Personal computers are used to control AGAS which allows zero gas, primary gas standards and the unknown secondary gas standard to be directed in rapid succession into the appropriate analyser. The AGAS then records the analysers response for each of the gases and subsequently uses these values to calculate the unknown secondary standards concentration, and other statistical information.

3.2.2 Experimental Procedure

The certification procedure involves bracketing the concentration of the secondary standard between adjacent concentrations of two primary gravimetric gas standards. It assumes that a linear algebraic interpolation of the analyser response can be made between the concentrations of these two standards. However, the responses of all analysers exhibit some non-linearity in their behaviour as a function of gas concentration. The magnitude of this non-linearity will depend both on the analyser employed and on the concentrations of the gases being analysed. Therefore, to allow for this, the response of each analyser is measured over the required range of concentrations be generating a four or five point calibration curve with appropriate known concentration standards.

The problem of analyser non-linearity is overcome by choosing the difference in the concentrations of the two bracketing standards to be small enough that the uncertainty in assuming a linear response is small compared with the uncertainty of the overall certification process. The concentrations of the bracketing standards are chosen to be within ± 4% of each other, with the concentration of the secondary standard between them, in order to produce an uncertainty of less than ± 0.1% of value. This procedure is verified regularly by comparing the analytical results obtained with sets of three NPL gravimetric standards with their gravimetric values.

4. UNCERTAINTY ANALYSIS

4.1 UNCERTAINTY OF THE GRAVIMETRIC PROCEDURE

The uncertainty in the accuracy of any given gravimetric standard is obtained from the uncertainties associated with the weighing procedure used to produce the standard, those which arise from the purity of the gases used and those from the relative molecular masses of its constituents. The uncertainty due to the sequential dilution process is also incorporated into the overall uncertainty budget.

4.1.1 Uncertainties arising from the Weighing Procedure

The sources of uncertainties arising in the weighing procedure have been grouped together into the following categories:

Balance Repeatability
Thermal Drift
Time Drift
Draught Instability
Location of Cylinder on Balance

Mass Piece Uncertainty
Resolution of Balance
Sensitivity of Balance
Buoyancy Correction
Expansion of Cylinder due to pressure
Mechanical Handling of Cylinder

Each of the categories have values assigned which were attained from experimentation. These value comprise both type A (the repeatability or randomness of a measurement process) and type B (those that account for errors that remain constant while the measurement is made) uncertainties. The probability distribution are determined for each of the categories and an appropriate devisor is then used.

4.1.2 Uncertainties arising from Gas Purity

Purity analyses are performed for all parent gases used in the preparation of both primary and secondary gas standards. These purity measurements are required by the Gravcalc software. The sequential dilution of one standard to produce the corresponding lower value in the hierarchical structure incurs a greater relative uncertainty as the concentration is reduced, so that the relative uncertainty increases each time a dilution is made. It is a necessary condition of the NPL uncertainty estimation procedure that the sum of all component mole fractions are equal to 1, and under these conditions it is assumed that perfect correlation applies.

4.1.3 Uncertainties arising from Component Relative Molar Masses

The relative molar masses of the gaseous components and the associated uncertainty in the relative molar masses are calculated from tables of atomic weights. The relative molar mass and uncertainties are combined with the gas purity and weighing uncertainty using the gravcalc software.

4.2 UNCERTAINTIES IN THE CERTIFICATION OF SECONDARY STANDARDS

In order to obtain a value for the concentration of a secondary standard, data from each of the standards, zero gas and unknown is collected sequentially from the AGAS system. The concentration of the secondary standard is then obtained from these results using the following formula:

$$X_{SS} = X_L + (X_H - X_L)\left[\frac{Y_{SS} - Y_L}{Y_H - Y_L}\right]$$

where X_L = concentration of low value NPL primary standard
X_H = concentration of high value NPL primary standard
Y_Z = stabilised analogue output for low concentration primary standard
Y_H = stabilised analogue output for high concentration primary standard
Y_{SS} = stabilised analogue output for secondary standard

This process is repeated between six and ten times (depending on the concentration of the mixtures and the stabilised uncertainty arising from the measurements) to form the mean value for the certified concentration of the secondary standard. Two such results are obtained on at least two different days with one pair of primary gas standards, and the complete procedure is repeated using a different pair of standards. The concentration of the secondary standard is then obtained by taking the mean of these four values.

The statistical uncertainty arising from the analytical measurement is derived from the automatic data collection procedure noted before. The AGAS computer performs a standard error analysis and produces both a mean and the standard error of the mean associated with that value. A computer program is used to combine the uncertainties from the primary gravimetric process with the uncertainties produced from the standard deviation of the instrument's response for each of the gas mixtures.

Thus, the uncertainty in the certification of the secondary standard s_x^2, is:

$$s_x^2 = \left(\frac{1}{R_2 - R_1}\right)^2 \left[(R_2 - X)^2 \; s_{R1}^2 + (X - R_1)^2 s_{R2}\right] + \frac{1}{(y_2 - y_1)^4}\left\{(y_2 - y_1)^2 s_y^2 + (Y - y_2)^2 s_{y1} + (Y - y_1)^2 s_{y2}^2\right\}$$

where

R_1 = Low Reference primary gas standard gravimetric value
R_2 = High Reference primary gas standard gravimetric value
X = Calculated concentration of secondary standard from Linear Interpolation
σ_{R1} = Gravimetric uncertainty of Low Reference gas
σ_{R2} = Gravimetric uncertainty of High Reference gas
y_1 = Instrument response to Low Reference standard
y_2 = Instrument response to High Reference standard
σ_{y1} = Standard deviation of the response of Instrument to low reference standard

σ_{y2} = Standard deviation of the response of Instrument to high reference standard
Y = Instrument response to secondary standard
σ_Y = Standard deviation of the response of Instrument to secondary standard.

Measurement anomalies due to non-linearities of the gas analysers have been determined and assigned a value of ± 0.1% relative (at 68% confidence level). These values are added to the combined standard uncertainties after correcting for probability distribution as square root sum of squares.

The expanded uncertainty U is obtained by multiplying σ_x by an appropriate coverage factor (k).

Thus $U = k\sigma_x$ and $X_{ss} \pm U$

Table 1 shows the expanded uncertainties at 95% confidence limit for NPL secondary standards.

TABLE 1

EXAMPLES OF NPL SECONDARY STANDARDS AND THEIR EXPANDED UNCERTAINTIES (95% CONFIDENCE LEVEL)

Nominal Conc	**Gas mixtures and their Expanded Uncertainties**					
	CO/N_2	**CO_2/ N_2**	**NO/N_2**	**C_3H_8/air**	**C_3H_8/ N_2**	**CH_4/ air**
7%	0.04%	0.04%	-	-	-	-
5%	0.03%	0.03%	0.03%	-	0.03%	-
2.5%	0.018%	0.018%	0.018%	-	0.018%	0.018%
1%	0.008%	0.008%	0.008%	0.008%	0.008%	0.008%
5000 ppm	40 ppm	40 ppm	40 ppm	40 ppm	40 ppm	40 ppm
2500 ppm	20 ppm	20 ppm	20 ppm	20 ppm	20 ppm	20 ppm
1000 ppm	8 ppm	8 ppm	8 ppm	8 ppm	8 ppm	8 ppm
500 ppm	4 ppm	4 ppm	4 ppm	4 ppm	4 ppm	4 ppm
250 ppm	2 ppm	2 ppm	2 ppm	2 ppm	2 ppm	2 ppm
100 ppm	0.9 ppm	0.9 ppm	0.9 ppm	0.9 ppm	0.9 ppm	0.9 ppm
50 ppm	0.5 ppm	0.5 ppm	0.5 ppm	0.5 ppm	0.5 ppm	0.5 ppm
10 ppm	0.1 ppm	0.1 ppm	0.1 ppm	0.1 ppm	0.1 ppm	0.1 ppm

5 RESULTS OF A TRIAL ROUND OF A PROFICIENCY TESTING SCHEME USING STACK EMISSION GASES

This section describes the results of the first round of a trial gaseous measurement proficiency testing scheme carried out by the National Physical Laboratory for the STA. Eighteen STA member companies took part in the scheme, which involved the round robin measurement of a number of traceable standard gas mixtures.

PT schemes provide a way of assessing the performance of laboratories by a series of regular inter-laboratory comparisons. In a typical PT scheme a test sample or material is sent for analysis to all participating laboratories. The results of the analyses are compared to assigned values of the samples. The assigned value may be a ‘true’ known value or in some cases, where a ‘true’ value is unknowable, it is based on the mean of all the results from the laboratories. The set of results are reported anonymously, and in addition each participant is made aware of their own results. In this way participants are able to assess their performance in relation to other laboratories. The key feature of a PT scheme is that it should be carried out regularly, and that a degree of improvement is then looked for in both poorly performing laboratories and in the overall performance of all participants.

In setting up a trial PT scheme for the STA it was decided to initially focus on measurements of gaseous components using continuous emission monitoring (CEM) equipment. This has the benefit that the test samples, in this case NPL standard gas mixtures, 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. A survey of interested STA members produced a target list of species and nominal concentrations. These are given in Table 2.

Table 2 : Sample gases used in trial PT scheme

Species	Nominal Concentration
CO in Nitrogen	2%, 1000ppm, 100 ppm
NO in Nitrogen	500 ppm
SO_2 in Nitrogen	1000ppm

Sixteen STA members returned results after participating in the scheme. In practice more than one sample of each gas was 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 2, but not the absolute value. The results of these analyses were returned to NPL. Participants were given the option to report the measurement uncertainty that they assigned to the results obtained. Not all participants took part in all tests and very few reported uncertainties.

The results of each analysis were expressed as percentage differences from the true value. This allowed 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 3. 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. 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 , thus

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

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. As an example, z scores have been calculated for the results obtained during this trial PT scheme. The values of uncertainty given in Annex 3 of the Hazardous Waste Incineration Directive have been used to derive σ. The z scores calculated from these are for example only, and a satisfactory score in this test should not be taken as compliance with the requirements of the Directive; the figures in the Directive were used purely to illustrate the use of z scores. Figure 2 summarises the z scores calculated in this way, and the results are given in Table 4. It can be seen that most results fall into the acceptable category, with only one analysis falling into the unacceptable category. If a z score approach is to be used in a subsequent ongoing PT scheme then target standard deviations should be agreed for all species tested.

The results of this trial PT scheme show the usefulness of such an exercise. However, for it to truly count as a PT scheme, with all of the associated benefits that that would bring, the scheme should run on a regular basis. This would enable STA members and others to monitor their own performance against their peers, and hopefully provide a regular incentive to strive for quality. Having a formally managed and approved PT scheme would also provide a demonstration of the commitment of participants to increased quality in their results.

Biographical Details: Paul Holland

Paul Holland is a research scientist and project manager in the Environmental Standards Section at the National Physical Laboratory. Paul currently manages a research project in which he is involved in developing new organic and inorganic gas standards. Other work at NPL has included the development of a continuous emission monitoring testing facility which is currently used for MCERTS testing. Prior to joining NPL, Paul studied for a Ph.D. in collaboration with BNFL developing novel radioactivity sensors using gaseous chemical interrogation methods.

Table 3. Percentage difference between reported results and NPL true value

Participant	2%CO	1000 ppm CO	100 ppm CO	500 ppm NO	1000 ppm SO2
a		-4.6 %	-0.9 %	-4.4 %	-0.4 %
b		0.3 %	-1.8 %	0.2 %	1.6 %
c					
d		0.6 %	1.2 %	3.4 %	13.3 %
e	-1.5%		-0.1 %	-1.1 %	
f		-4.6 %	-1.6 %	-1.0 %	
g			2.8 %	-1.1 %	
h		-0.9 %	-1.4 %	-5.2 %	1.3 %
I				-0.2 %	1.0 %
j	0.5%	0.1 %	0.2 %	0.0 %	0.2 %
k	-6.4 %	4.1 %	4.8 %	-1.9 %	-3.5 %
l			2.8 %	0.6 %	-3.4 %
m		3.1 %	3.7 %	13.1 %	-32.2 %
n		1.8 %	1.8 %	-2.8 %	-0.2 %
o		-0.7 %	-0.5 %	4.9 %	
p					
q	-8.9 %	-8.3 %	-0.1 %		
r		-4.3 %	-6.9 %	1.2 %	-4.7 %

Table 4. Z Scores

Participant	2% CO	1000 ppm CO	100 ppm CO	500 ppm NO	1000 ppm SO_2
a		-0.92	-0.18	-0.44	-0.04
b		0.05	-0.36	0.02	0.16
c					
d		0.11	0.25	0.34	1.33
e	-0.30		-0.02	-0.11	
f		-0.91	-0.33	-0.10	
g			0.56	-0.11	
h		-0.18	-0.28	-0.52	0.13
I				-0.02	0.10
j	0.10	0.02	0.04	0.00	0.02
k	-1.28	0.82	0.95	-0.19	-0.35
l			0.56	0.06	-0.34
m		0.62	0.74	1.31	-3.22
n		0.36	0.36	-0.28	-0.02
o		-0.13	-0.10	0.49	
p					
q	-1.77	-1.66	-0.02		
r		-0.87	-1.38	0.12	-0.47

Figure 1 : Summary of results of STA PT scheme for gaseous analysis

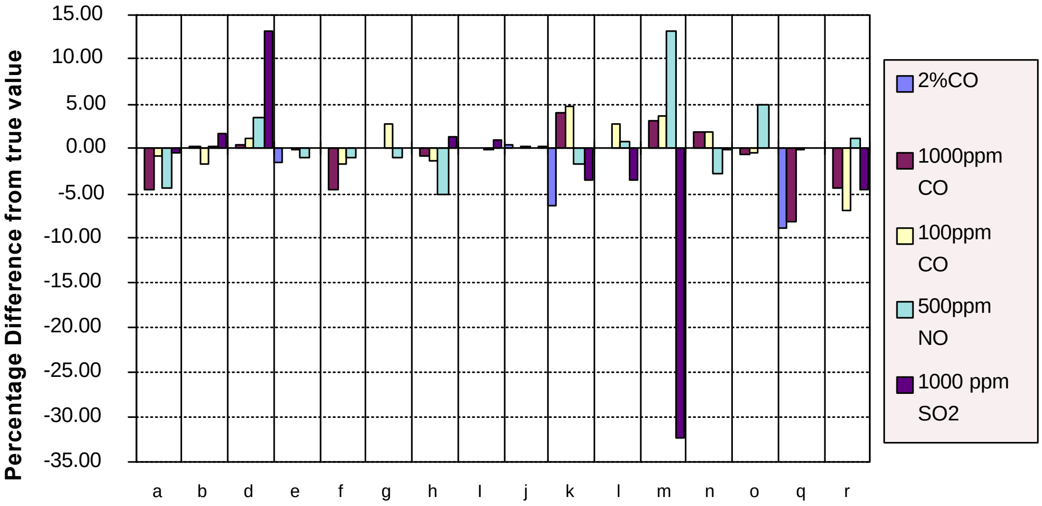

Figure 2: Z Scores for STA PT scheme for gaseous analysis