

A Unique Stack Simulator Facility at the National Physical Laboratory:

Case Studies of an NPL Calibration Transfer Strategy for Mass Spectrometers and a Trial of a Proficiency Testing Scheme with Source Testing Association Members

Abstract

We report the capabilities of a Stack Simulator facility developed at the National Physical Laboratory (NPL) and describe its use in two case studies involving the testing of an NPL calibration transfer strategy for process control mass spectrometers and the trial of a Proficiency Testing (PT) scheme. In the former it was shown that under real stack conditions the calibration transfer strategy improved the quantitative accuracy of a Quadrupole Mass Spectrometer (QMS) from an error of 70 % down to 4 %. In the trial of a PT scheme involving four Source Testing Association (STA) members it was found that three of the members could quantify NO/O₂/CO/SO₂ test mixtures to within the requirements of the Waste Incineration Directive (WID) whilst the fourth could not, reporting an SO₂ concentration in error by -26 %. The error source was traced back to a bias in the members' calibration gas.

Stack Simulator Facility

Figure 1 ►
Schematic of external (a) and internal (b) components of the National Physical Laboratory Stack Simulator facility. Specifications include; four 5" BSP sample ports (v), stack velocities of 12 m s⁻¹ due to the centrifugal fan (w), stack temperatures of up to 200 °C due to internal heaters (z) and water vapour concentrations of up to 25 % by volume. The flow restriction (x) ensures a constant velocity across a duct of uniform cross-section (y). (c) The portable European Spectrometry Systems ECO-Sys-p quadrupole mass spectrometer used with the stack simulator to test the calibration transfer strategy from case study 1. (d) The stack simulator in use.

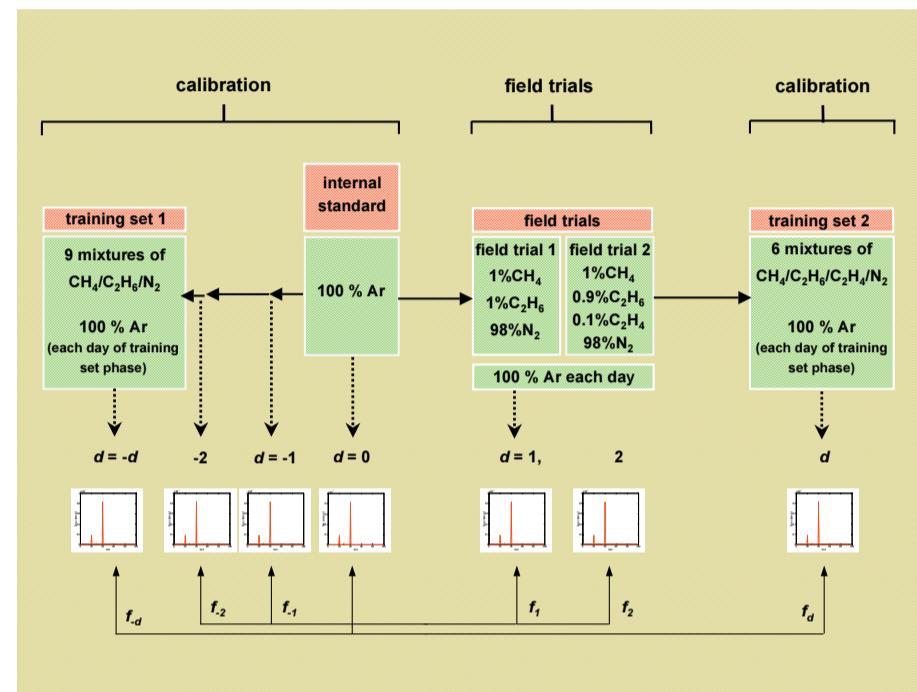
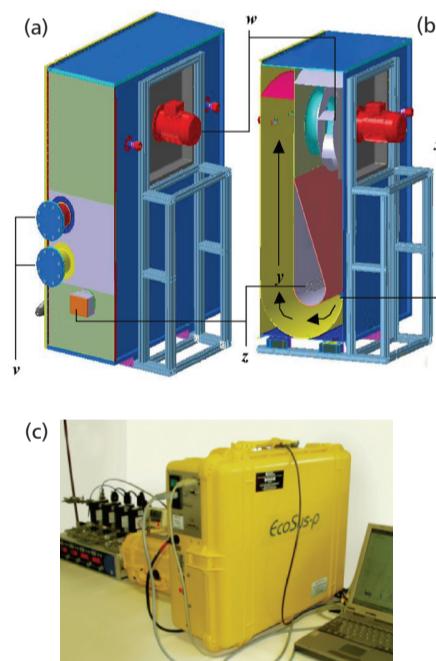


Figure 2

Schematic of all field trial and calibration measurements. Ethylene is included as an "unexpected" species in field trial 2 in order to demonstrate the effects on calibrations based on training set 1. When the calibration transfer strategy is employed to compensate for instrumental drift all spectra are scaled to day zero (d_0) by factors (f_d) determined from changes in recorded spectra of the pure argon internal standard.

The Stack Simulator facility developed at the National Physical Laboratory allows instrument manufacturers and stack monitoring companies to test equipment and procedures over a range of typical field operating conditions.[1] Furthermore, the capability to generate compositions at field typical flows and temperatures in a chamber built as a simulator of a 1.5 m diameter stack enables proficiency testing of company personnel and methods.

The simulator has a cross-stack path length of 1.5 m and a capacity of 300 L (Fig. 1). There are four 5" BSP ports arranged as opposing pairs to allow cross-stack as well as extractive sampling. In principle, test gas mixtures can be created to simulate any process or emissions measurement problem. Gases are re-circulated with a centrifugal fan creating a high vertical stack velocity whilst enabling low gas consumption and low releases to atmosphere. A flow restriction ensures a constant velocity across a duct of uniform cross section.

Calibration Transfer Strategy

The principle of the calibration transfer strategy is to adjust the field and calibration spectra so that they appear as though they were all recorded on the same day (ie. any effects from instrumental drift are removed). This is achieved by measuring pure argon as an internal standard. A day zero is arbitrarily chosen (Fig. 2) and the argon internal standard measurements are used to calculate drift correction factors (f_d) for each day, from:

$$f_d = \frac{1}{2} \left(\frac{\text{Ar } P_0^{20}}{\text{Ar } P_d^{20}} + \frac{\text{Ar } P_0^{40}}{\text{Ar } P_d^{40}} \right)$$

where $\text{Ar } P_0^{20}$ and $\text{Ar } P_d^{20}$ represent the QMS response at $m/z=20$ for pure argon at days zero and d , respectively, and $\text{Ar } P_0^{40}$ and $\text{Ar } P_d^{40}$ represent the analogous QMS responses at $m/z = 40$. Every spectrum recorded on day d being scaled by this factor to correct for the effects of instrumental drift.

QMS Measurement Protocol

Calibration Phase

- Power up instrument pumping system, ion source and detector electronics
- Stabilisation for a suitable time period (for some models 48 h may be necessary)
- Flush through internal standard. System stability is confirmed if the response to the parent ion / most intense peak does not drift by more than 0.02 % min⁻¹
- Measure ten spectra of the internal standard and calculate the mean
- Measure calibration samples repeating steps (c) – (d) for each day of the calibration phase

Field Trial Phase

- If instrument has been powered down

repeat steps (a) to (d), otherwise repeat steps (c) to (d)
 (g) Carry out field trial measurements using same instrumental configuration as for calibration phase. For each day of the field trial campaign carry out steps (c) to (d)

Quantification

- (h) Define day zero (d_0), determine daily correction factors (f_d) and apply to all calibration and field trial spectra to compensate for instrumental drift
- (i) Using corrected calibration spectra train desired calibration (e.g. classic least squares) and use to quantify corrected field trial spectra

Discussion

Field trial 1 represents the scenario where all the species encountered on a site (methane and ethane) are present in the calibration. Using training set 1 without calibration transfer the predictions for methane and ethane are 0.83 and 0.70 % mol mol⁻¹, respectively, compared to GC determinations of 0.94 and 0.95 % mol mol⁻¹ (results not shown). The under-prediction is a result of instrumental drift between collection of the training set and collection of the field trial data. After applying the calibration transfer strategy, accuracy is significantly improved with predicted concentrations for methane and ethane of 1.04 % mol mol⁻¹ and 0.89 % mol mol⁻¹, respectively.

In field trial 2 the scenario is simulated where an additional unexpected species (ethylene) is present at the site that was not included in the original calibration. In the absence of the calibration transfer strategy the predictions for methane and ethane are 1.06 and 1.25 % mol mol⁻¹, respectively, compared to GC determinations of 0.93 and 0.82 % mol mol⁻¹. The marked over-prediction of the latter is explained by cross-interference of the ethylene with many of the ethane fragments.

Presented with such a scenario a typical response would be to post calibrate the instrument for ethylene, re-train the CLS and re-interpret the spectra acquired during the field trial. In doing this it is seen that there is no improvement and overall the accuracy has actually become poorer (Fig. 3a). This is due to the time gap between recording the training set containing methane and ethane (training set 1) and the set containing ethylene (training set 2). Across this time the instrument has drifted and hence the responses to methane and ethane fragments for the same concentration will appear altered between the two sets. Consequently, this provides the CLS algorithm with conflicting calibration information degrading the subsequent quantification.

Extending the calibration transfer strategy to correct for drift across both training sets and field trial 2, re-training the CLS algorithm and re-interpreting the spectra yields significantly improved accuracy (Fig. 3b). Now the concentrations of methane and ethane can be determined to within an accuracy of 4 % and 10 %, respectively.

These data demonstrate that the calibration transfer strategy can be successfully utilised to not only improve the performance of multi-variate calibrations from the lab when taken into the field, but also enable post calibration to be carried out without any loss of quantitative accuracy.

Case Study 2: Trial of a Proficiency Testing Scheme for STA Members

For plant operators to demonstrate that emissions meet the requirements of Integrated Pollution Prevention and Control (IPPC) licenses there must be confidence in the monitoring data. A key element that allows stack-testing companies to facilitate customer confidence and show the validity of their measurement systems and competence of staff are Proficiency Testing schemes. Previously PT schemes have been carried out

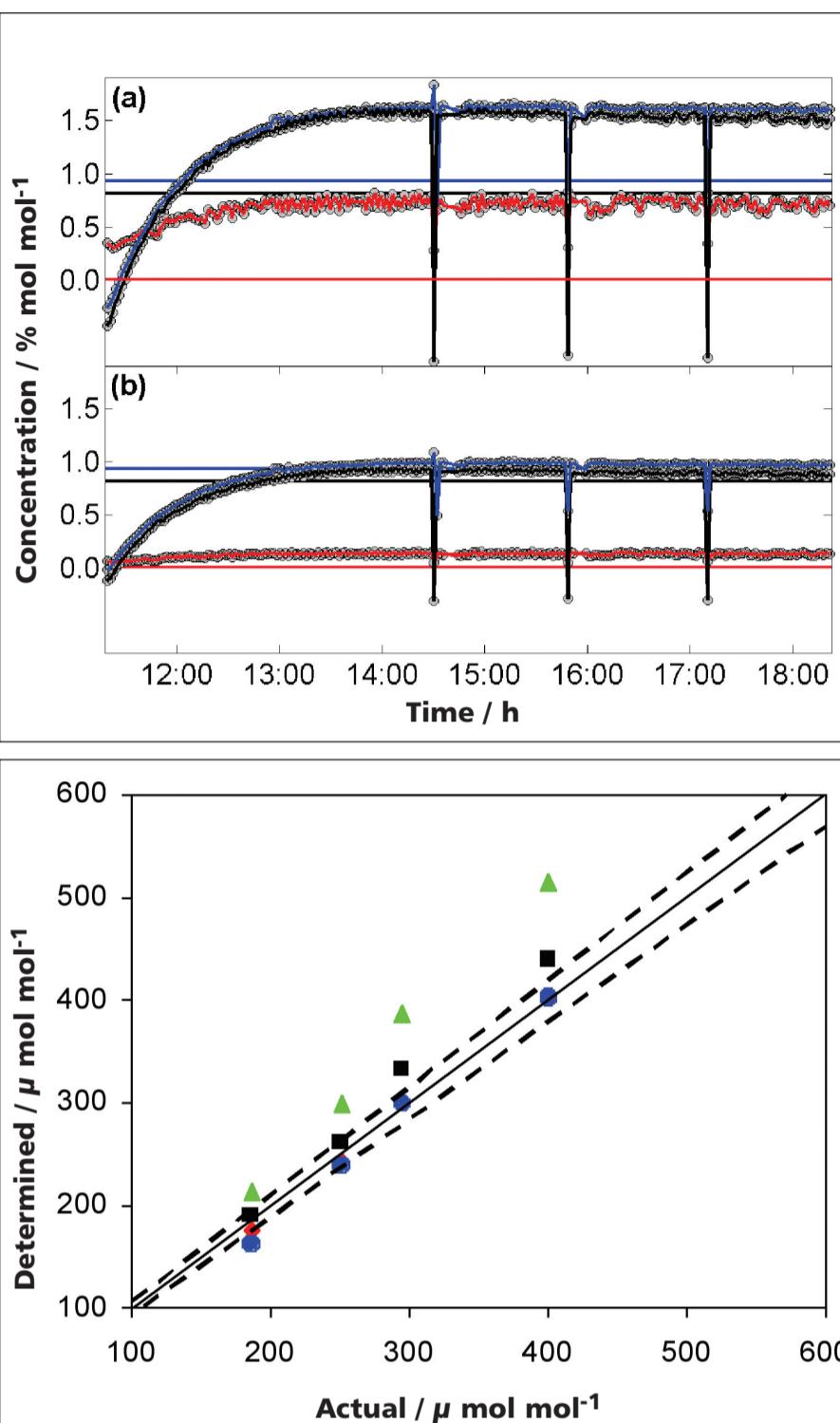
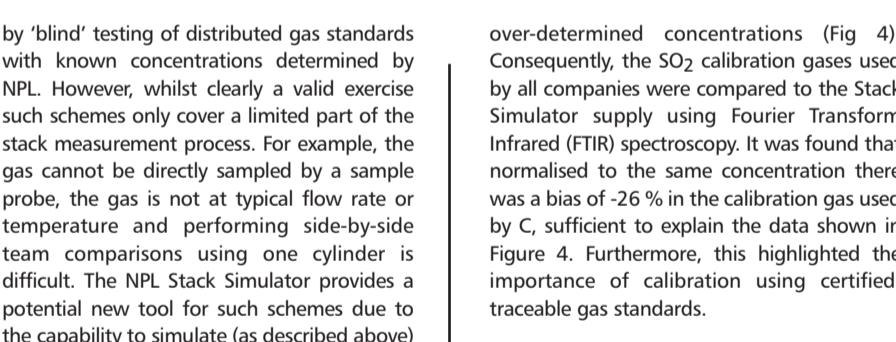


Figure 3
 Predicted concentrations of CH₄ (●), C₂H₆ (○) and C₂H₄ (■) from a CLS analysis trained using combined training sets 1 & 2) of field trial 2 data without (a) and with (b) the calibration transfer strategy. The gas was sampled from the stack simulator at 60 °C using a method 5 pumping system. The “true” concentrations of CH₄ (—), C₂H₆ (—) and C₂H₄ (—) are determined from a GC analysis of samples collected in evacuated 10 L cylinders from the stack simulator against NPL primary reference materials. 24 h prior to the field trial the QMS system was power cycled to simulate travel to the customer plant.



by ‘blind’ testing of distributed gas standards with known concentrations determined by NPL. However, whilst clearly a valid exercise such schemes only cover a limited part of the stack measurement process. For example, the gas cannot be directly sampled by a sample probe, the gas is not at typical flow rate or temperature and performing side-by-side team comparisons using one cylinder is difficult. The NPL Stack Simulator provides a potential new tool for such schemes due to the capability to simulate (as described above) conditions typically encountered on site.

In order to demonstrate the suitability of the Stack Simulator for a PT scheme a trial was organised in conjunction with the Source Testing Association (STA) involving four stack testing companies (labelled A to D). A range of certified gases typical of combustion processes were generated in the simulator. These were composed of mixtures of NO/SO₂/O₂/CO at a velocity of 10 m s⁻¹ and a temperature of 450 K. Four concentration step changes were made across the test period. The four companies were provided only with nominal composition and condition information to aid calibration of the Horiba analysers that were employed by all, otherwise the tests were ‘blind’. All companies arrived with full field kit and sampled using the four 5” BSP ports provided on the simulator.

Concentrations of NO, O₂ and CO were correctly determined by all stack testing companies to within an uncertainty of \pm 10 %. However, with regard to SO₂ only companies A, B and D could meet the requirements of the Waste Incineration Directive with C reporting significantly

over-determined concentrations (Fig. 4). Consequently, the SO₂ calibration gases used by all companies were compared to the Stack Simulator supply using Fourier Transform Infrared (FTIR) spectroscopy. It was found that normalised to the same concentration there was a bias of -26 % in the calibration gas used by C, sufficient to explain the data shown in Figure 4. Furthermore, this highlighted the importance of calibration using certified, traceable gas standards.

Conclusions

Using the unique Stack Simulator facility at NPL it has been shown that the error in the quantitative accuracy of a mass spectrometer aimed at process control applications can be reduced from 70 to 4 % by using a calibration transfer strategy. Moreover, it has been shown that using the strategy it is possible to include post calibration spectra in a chemometric training set without losing quantitative accuracy. Previously, if encountering a species on site not in the original calibration it would have often been necessary to re-measure the entire training set in order to include the additional component, or else risk losing quantification accuracy.

The trial of a PT scheme using the Stack Simulator demonstrated the potential of such a scheme to improve the quality of stack sampling results. It was found that three of the members could accurately determine the concentrations of all four test species (NO/SO₂/O₂/CO), whilst the fourth was found to be inaccurate by -26 % for the SO₂ determination, an error which was traced back to a bias in the members’ calibration gas.

Figure 4
 SO₂ concentrations determined by stack testing companies A (■), B (◆), C (▲) and D (●) as a function of actual SO₂ concentration (solid line) present in four different compositions of NO/SO₂/O₂/CO generated on NPL’s Stack Simulator facility at 10 m s⁻¹ and 450 K. Uncertainty of generated SO₂ concentration in simulator (dashed lines).

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References

- [1] <http://www.npl.co.uk/environment/stack/>

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