

Online Mass Spectrometry - A Method for Future Emission Monitoring?

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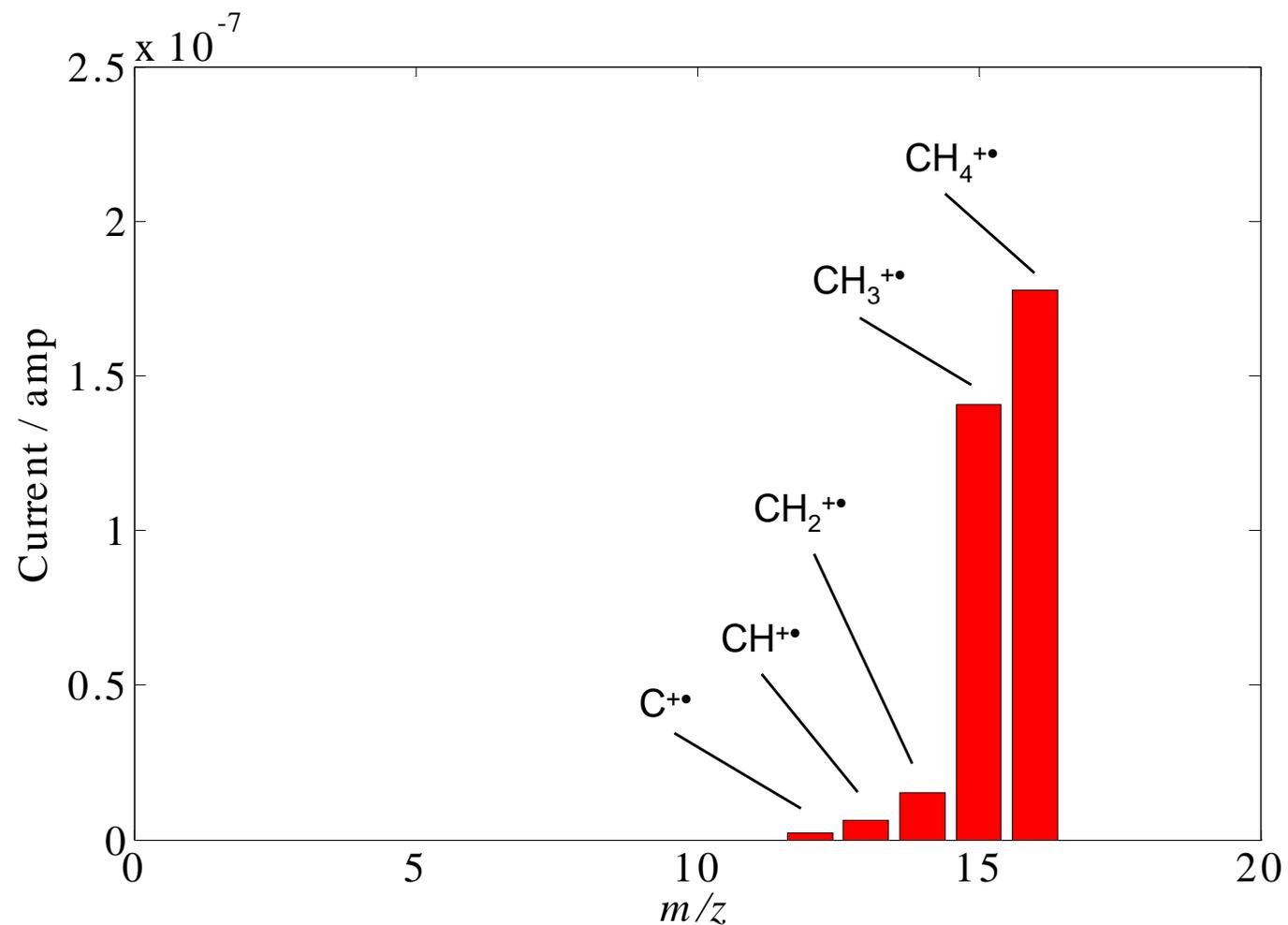
- Introduction to mass spectrometry
- Potential benefits of using QMS for process/emissions monitoring applications
- Effect of instrumental drift on quantitative analyses
- Using a Calibration Transfer Strategy to correct for the effects of drift
- Testing the strategy using NPL's Stack Simulator

Principles of Mass Spectrometry

- If a molecule, or atom, is bombarded with electrons it can be ionised
 - $\text{CH}_4 + e^- \rightarrow \text{CH}_4^{+\bullet} + 2e^-$
- The path of ions can be controlled by electric and magnetic fields
- Consequently, this provides a means by which to separate ions
- By sequentially changing the electric/magnetic field it is possible to separate out and detect in turn each ion present in a sample, building a mass spectrum
- However, an added advantage of mass spectrometry is that during the ionisation process chemical bonds may be broken creating smaller fragment ions
 - *e.g.* $\text{CH}_3^{+\bullet}$, $\text{CH}_2^{+\bullet}$, *etc.*
- This creates (in most cases) a unique mass spectral pattern which facilitates identification and quantification

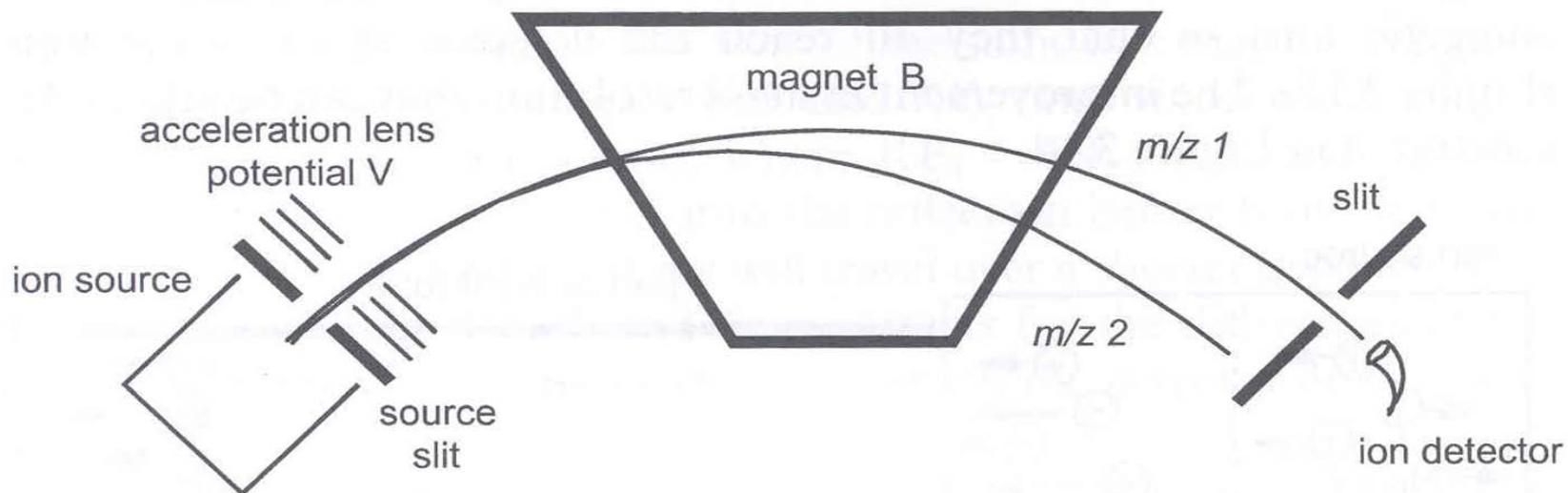
Example Mass Spectrum of CH₄

- *nb.* As CH₄⁺ has the same mass as the CH₄ from which it was produced, this is often called the parent ion

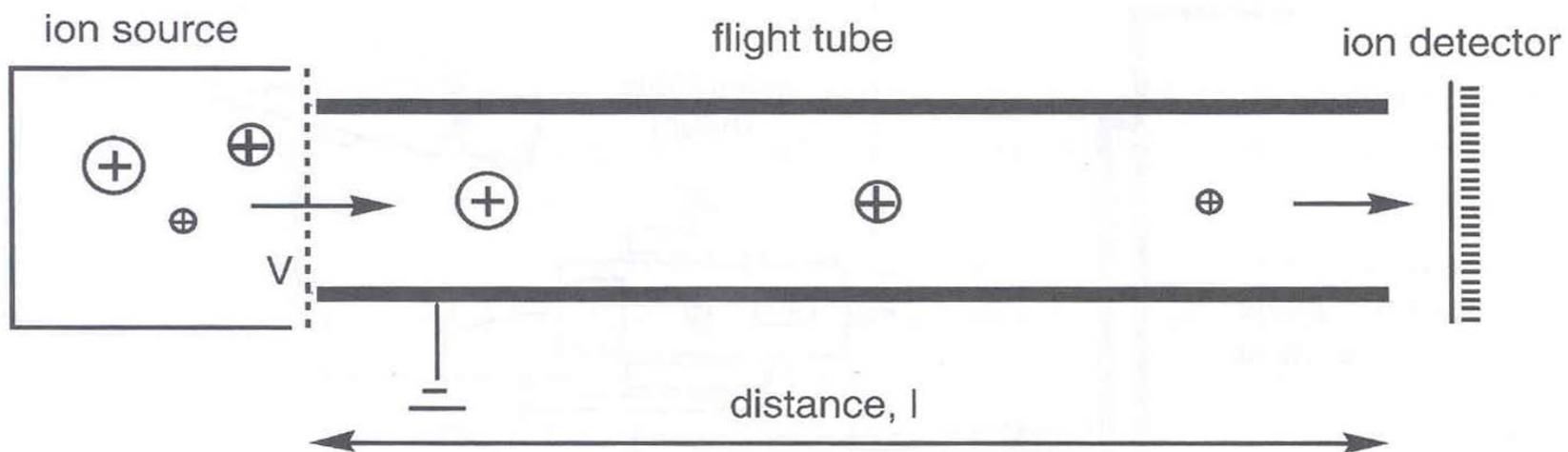


Some Common Types of Mass Spectrometer

- Magnetic Sector

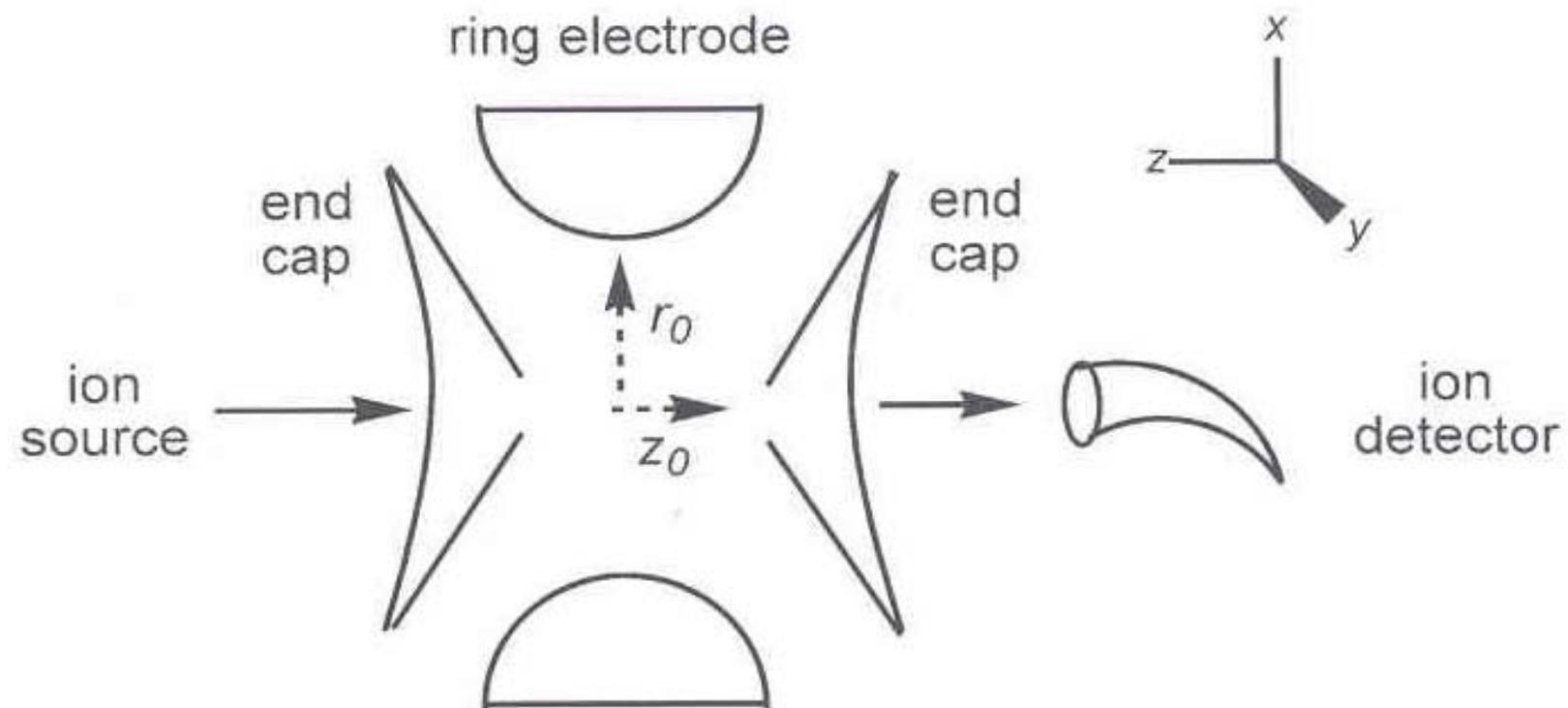


- Time of Flight (TOF)



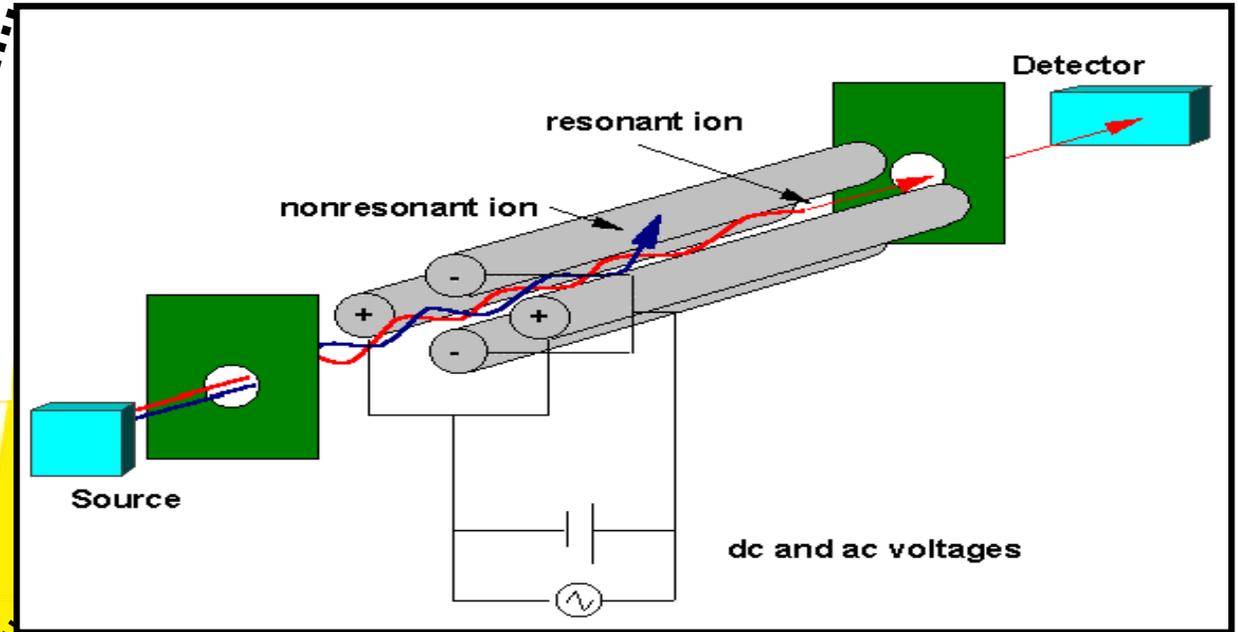
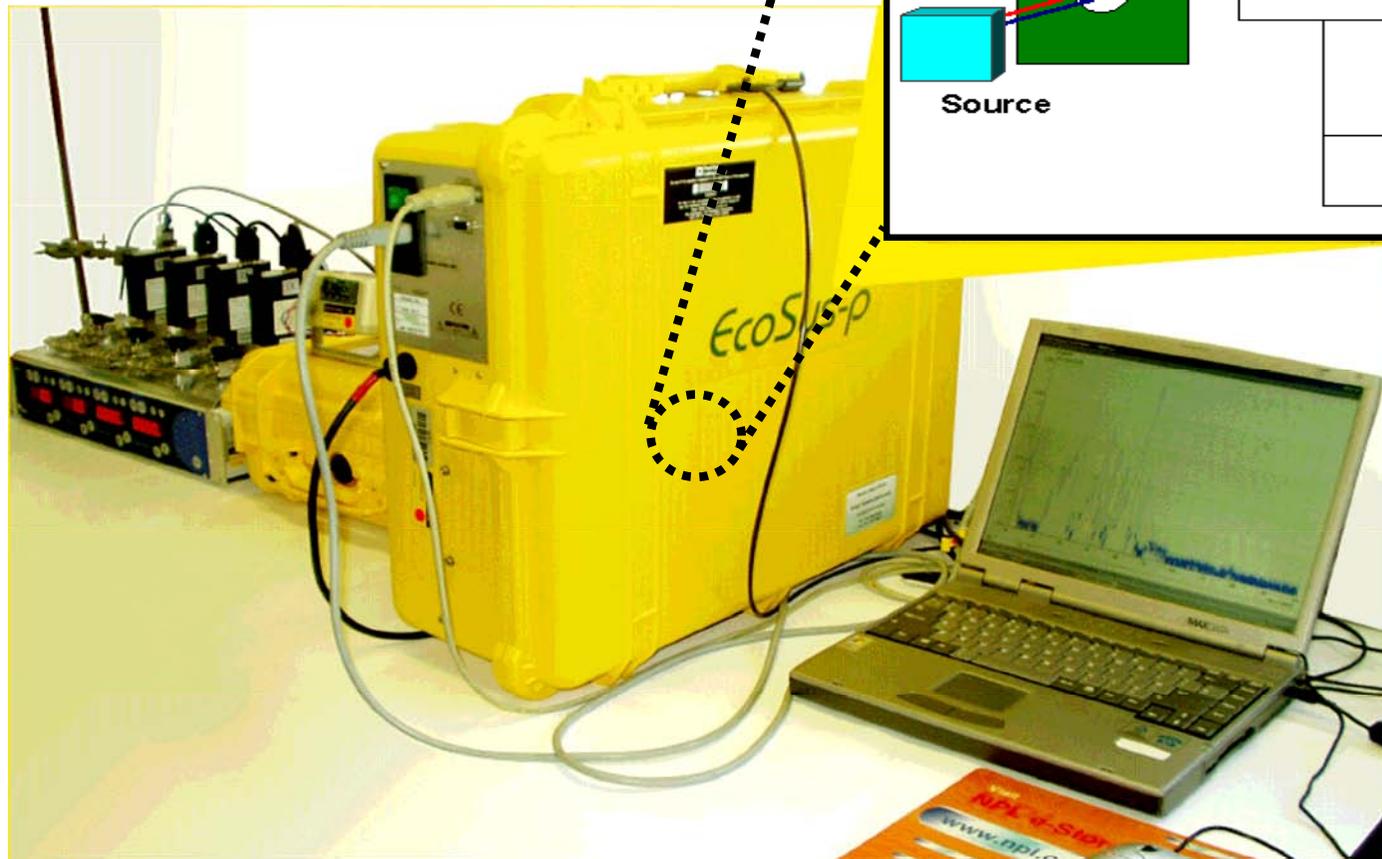
Some Common Types of Mass Spectrometer

- Ion Trap (IT)



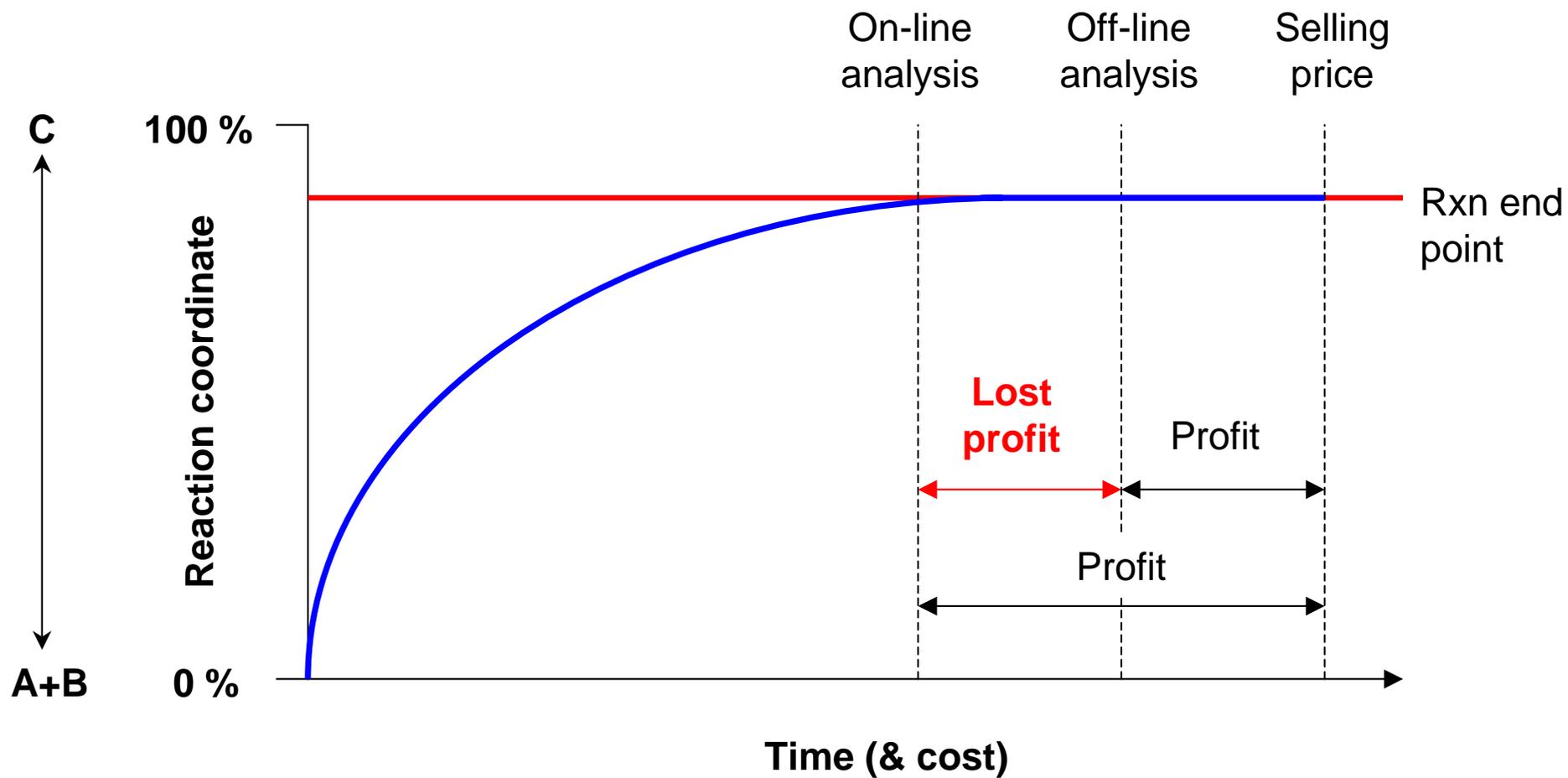
Portable Quadrupole Mass Spectrometer (QMS)

- Portable suitcase design QMS



- Less expensive than magnetic sector or IT mass spectrometers
- Similar priced TOF suitcase mass spectrometers available. But can suffer from similar drift issues

Economic Benefits of Real-Time, On-Line Process Monitoring



Where is QMS Applicable?

- Petrochemical industry: Ethylene cracking plant
 - Plant generally consists of a number of cracker furnaces monitored by a series of GC's
 - GC run times being ~60 mins
 - Temperature, pressure and flow measured in real time to predict yields (Model Based Control) which are validated by subsequent GC measurement
 - If predicted and validated yields (model vs GC measurement) deviate furnace operator intervenes....**60 mins too late!**
 - **A typical plant could save an estimated \$4 million through real-time monitoring**

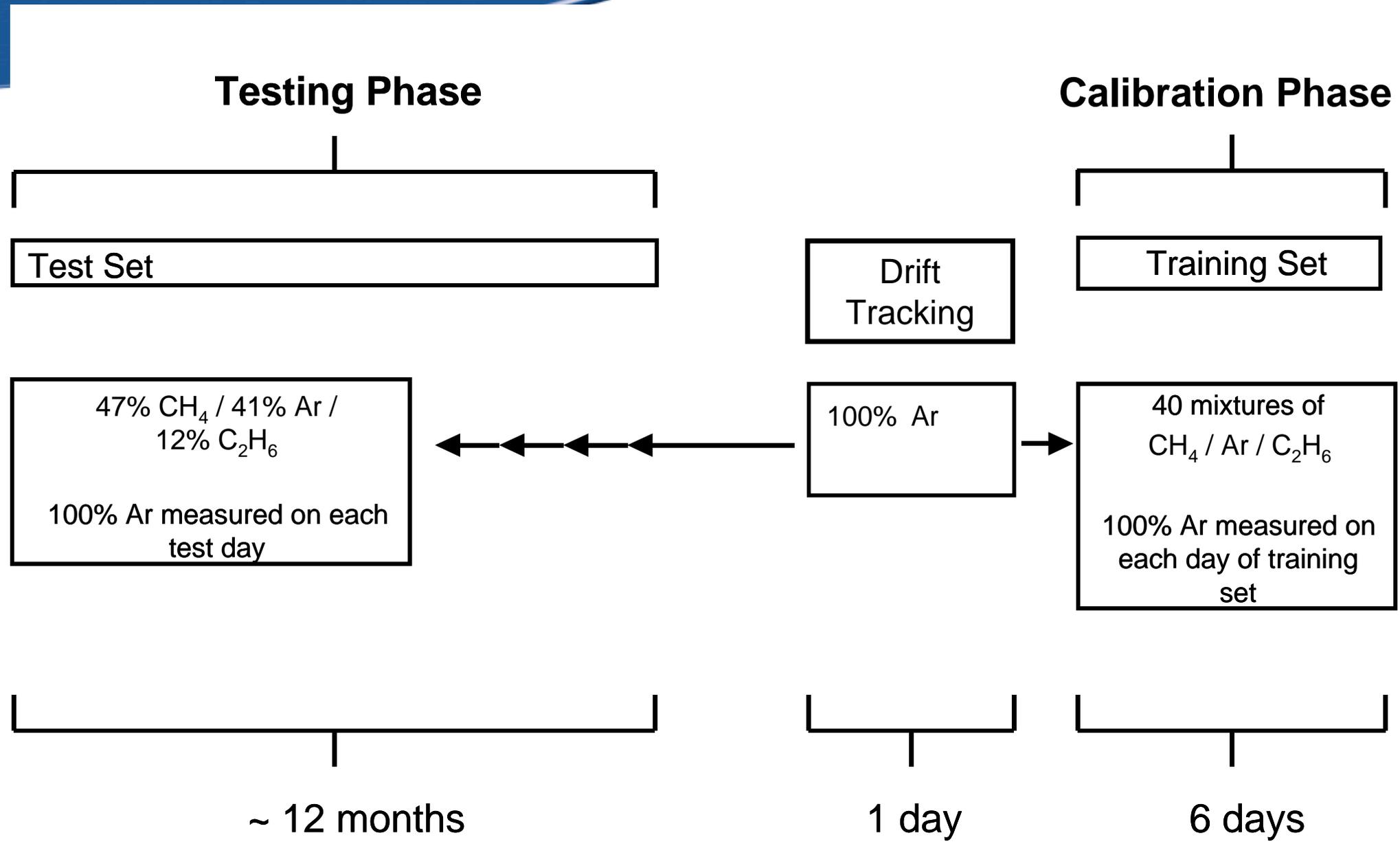
Advantageous & Disadvantageous of Portable QMS

| Advantageous | Disadvantageous |
|---|---|
| On-line, real-time monitoring | Instrumental drift |
| Simultaneous detection of multiple species | Have to deconvolve complex spectral patterns (but software is available) |
| Wide dynamic range (potentially applicable to process and emissions measurements) | Membrane inlet often used on ppb range excluding some species (but sometimes could be an advantage) |
| Cheaper than other forms of MS, entry level ~£20k | More expensive than impinger train! |
| Can automate operation | Staff need training before use |

Characterising QMS Instrumental Drift and using Calibration Transfer to Compensate

- To realise the multiple species capability of QMS it is often necessary to calibrate with many multi-component gas standards
 - Expensive
 - Time consuming (will often take a number of days)
- Due to instrumental drift large quantification errors can appear in weeks or even days after calibration
- Isn't economically viable or practical to re-calibrate on this time scale
- Consequently, for QMS to have a future in process/emissions monitoring for quantitative analysis this must be addressed

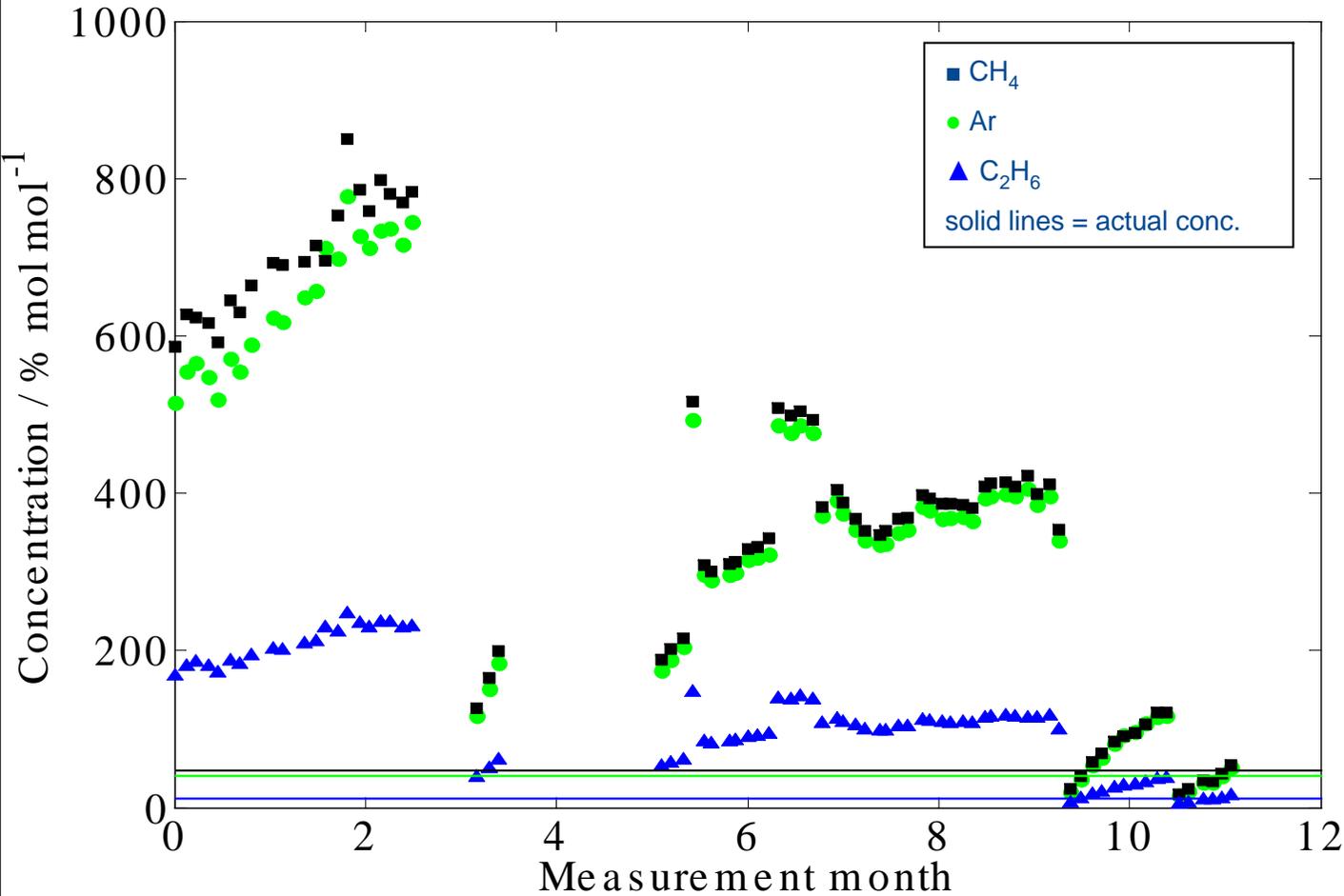
Laboratory Dataset Schematic



Quantification of Drift

- Quantifying test set spectra using training set spectra for instrument calibration

| Data Point | Perturbation |
|-----------------|--|
| 22 | Instrument power cycle |
| 25 | Measurement gap |
| 28 | Electron energy decrease from 100 to 70 eV |
| 36, 37, 38 & 39 | Electron energy decrease from 100 to 85 eV |
| 63 | Non-user induced sensitivity decrease |
| 74 | Non-user induced sensitivity decrease |



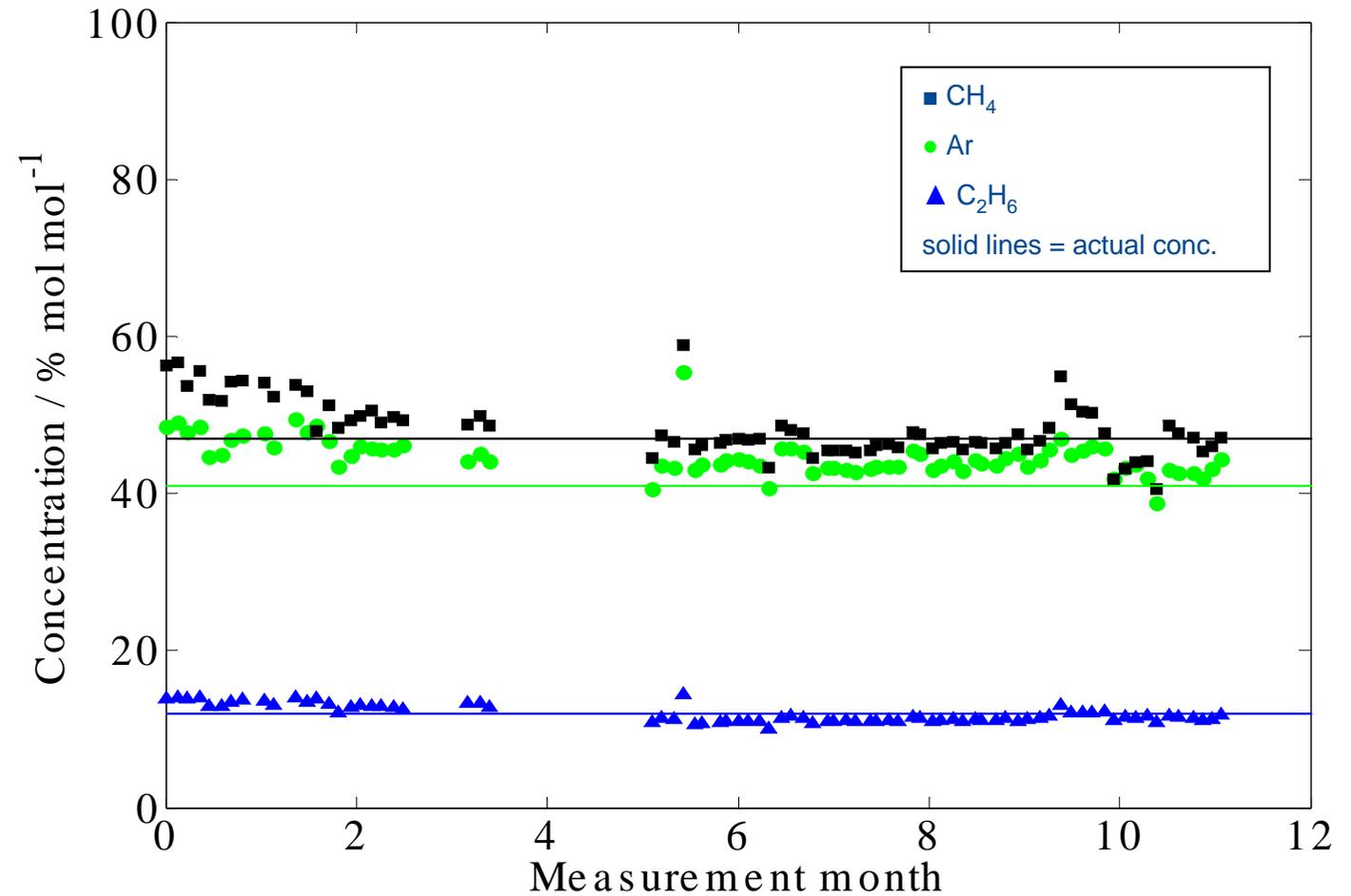
The Principle of Calibration Transfer

- The principle of calibration transfer is to adjust spectra to appear as though they were all recorded on the same day
- We have experimented with various approaches (e.g. adjusting spectra based on measuring change in instruments electron energy) and this is the subject of ongoing work
- However, thus far we have shown that significant improvements in quantitative accuracy can be found by using a relatively straightforward approach

- To compensate for the effects of drift in a spectrum
 - Decide one day to correct all spectra to
 - Compare Ar measurement on that day to first test set day and calculate correction factor
 - Product of factor with test set spectrum yields transferred test set spectrum
 - Repeat for all subsequent days

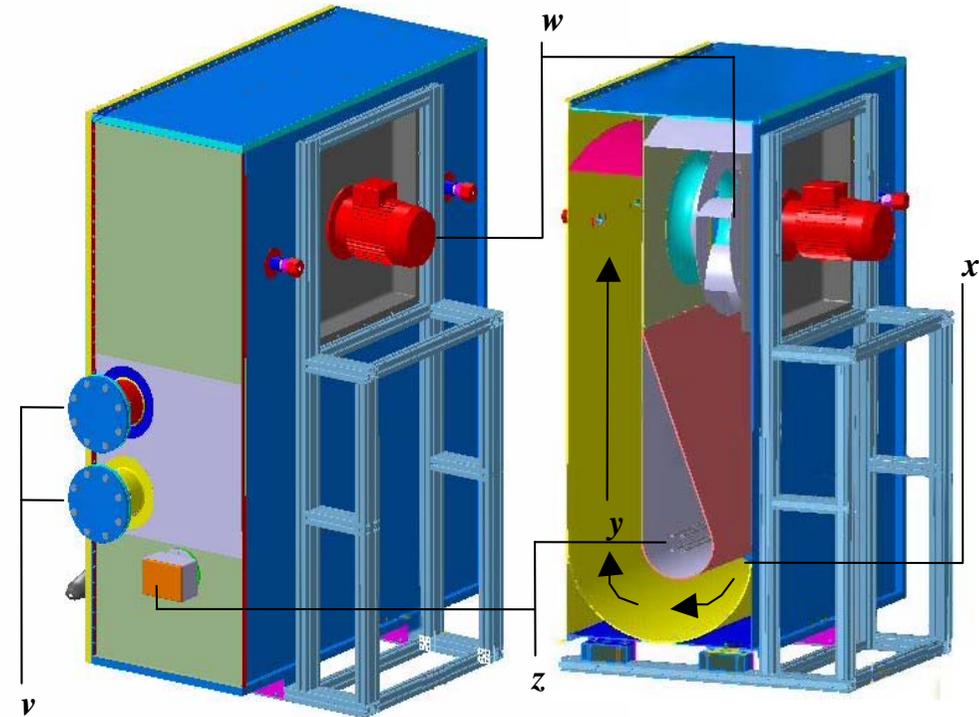
Quantification when Employing the Calibration Transfer Strategy

- Errors seen in quantification after two weeks in the absence of a calibration transfer strategy now do not appear for ~11 months



Testing QMS and Calibration Transfer Strategy on NPL's Stack Simulator Facility

The Stack Simulator Facility



- Facility designed for testing of instrumentation, staff training and PT schemes
- 1.5 m cross-stack, 300 L capacity, four 5" BSP sample ports (v)
- Capable of generating a broad range of gas mixtures, including up to 25% water vapour
- Velocities up to 12 ms^{-1} due to a centrifugal fan (ω)
- Temperatures up to $200 \text{ }^\circ\text{C}$ (z)

Small Digression (1) - Stack Simulator

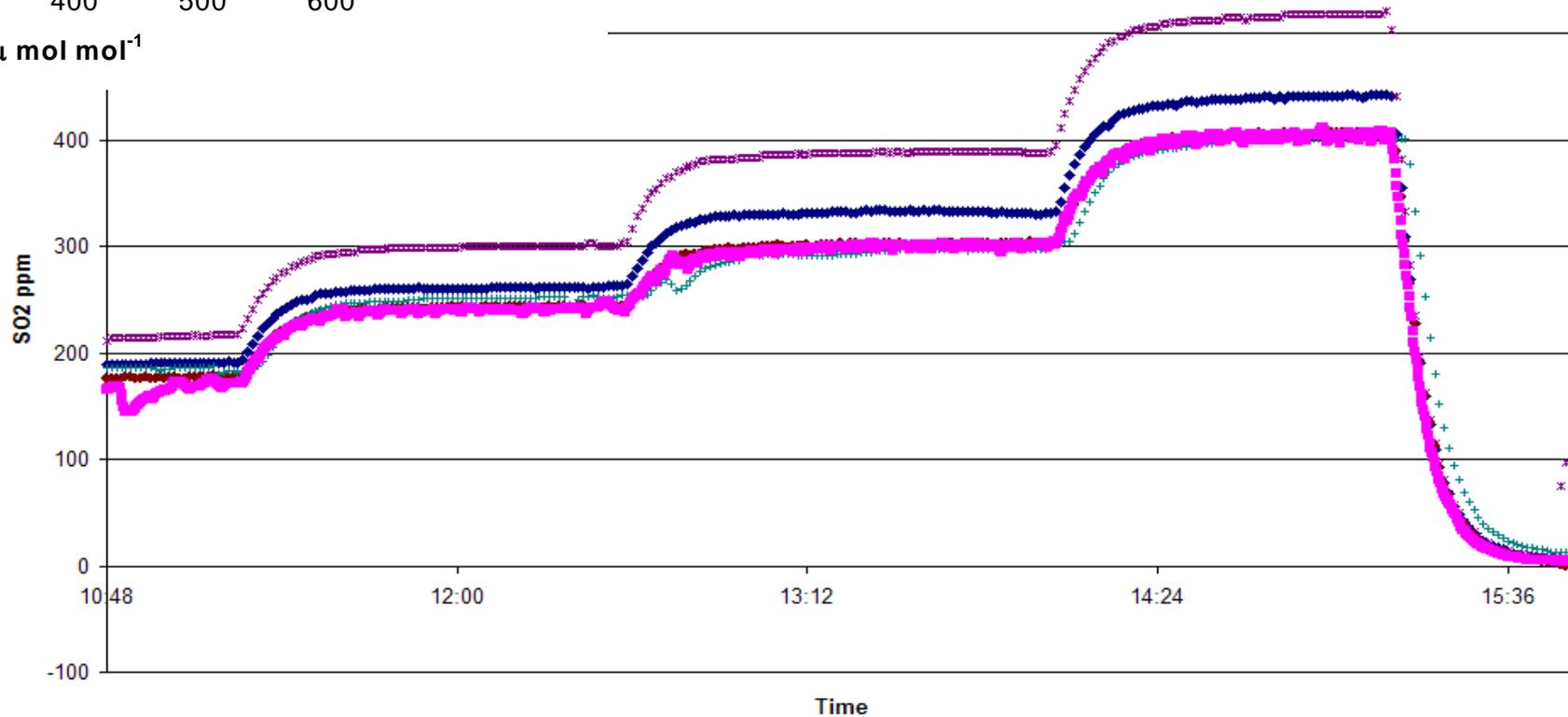
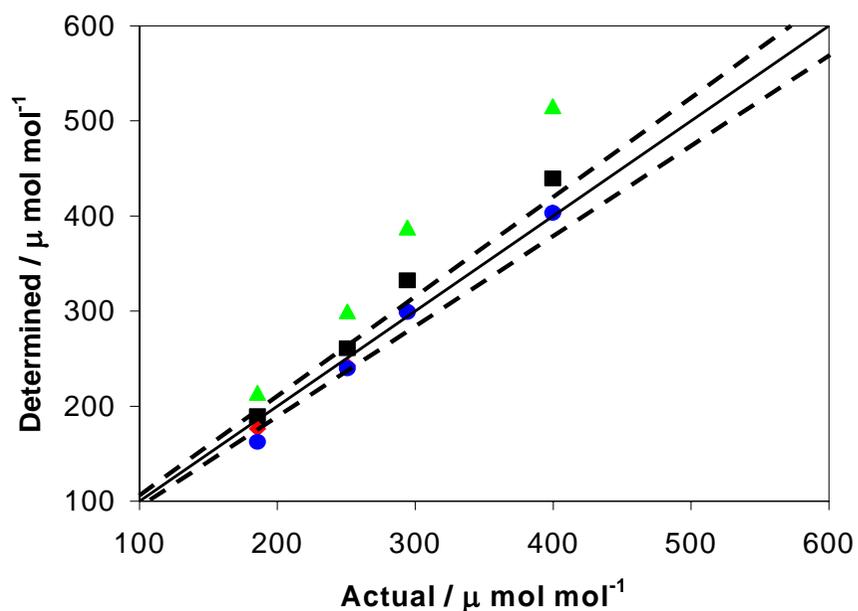
Trial of a PT Scheme

- Four STA members anonymously took part in a trial of a PT scheme
- Tested with mixtures of
 - CO, O₂, SO₂, NO
 - with four step changes in concentration
- Concentrations referenced using FTIR
- Particulates next



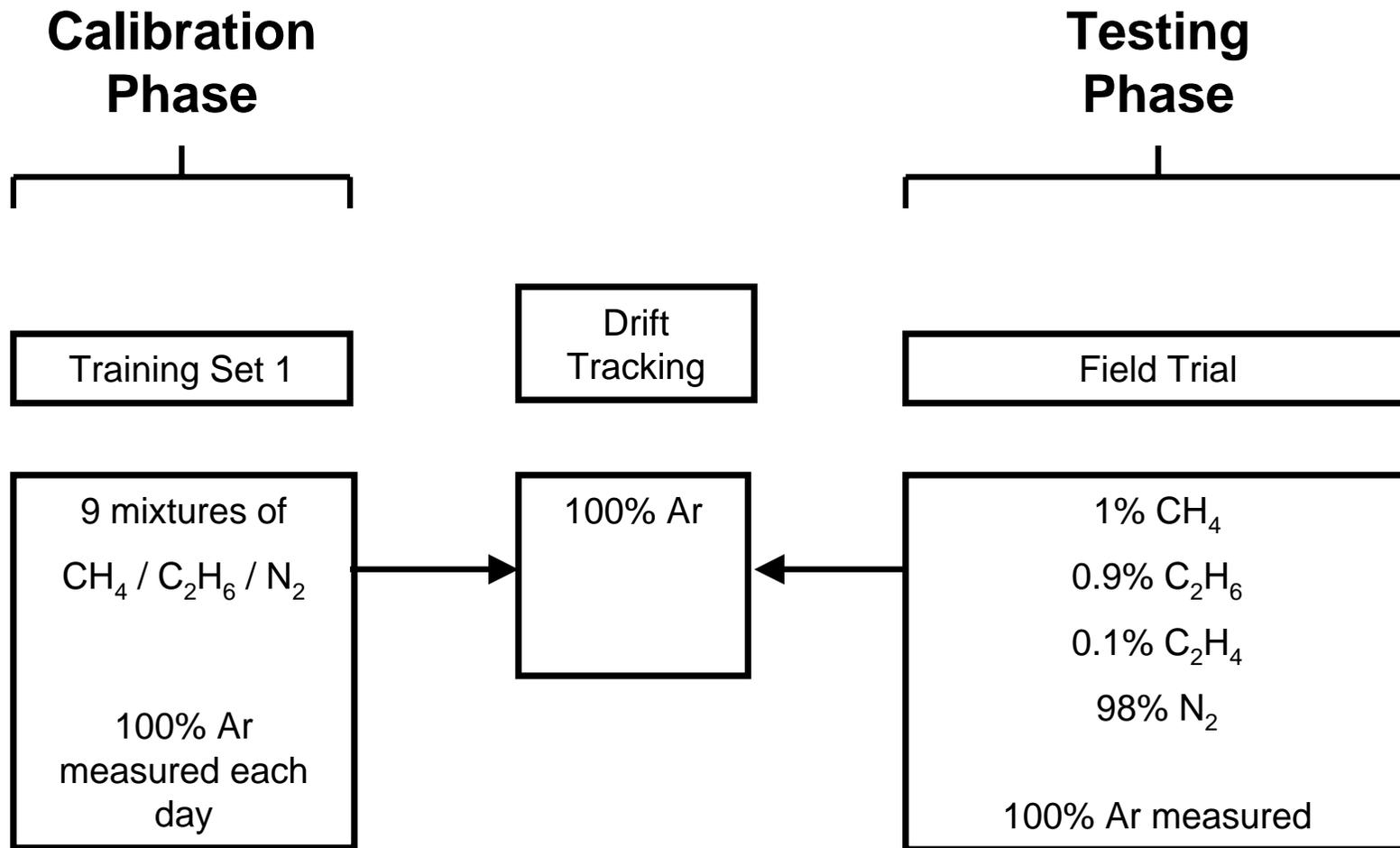
Small Digression (2): Results for SO₂

- Company (▲) could not quantify SO₂ to requirements of WID
- Problem traced back to error in calibration standard
- [see Spring 2007 issue of International Environmental Technology for further info]

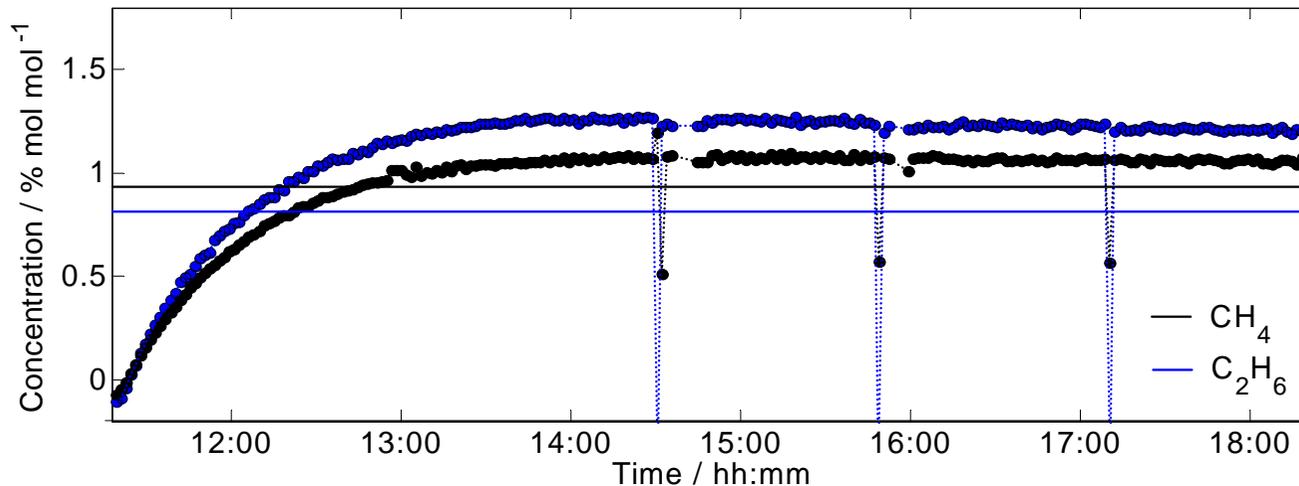


- Data set designed to
 - (a) Show the effect when a species not included in the calibration is present on the field trial
 - (b) Show the problems of trying to post calibrate for an “unexpected” species when using a multi-variate approach

Field Trial Data Set (1)



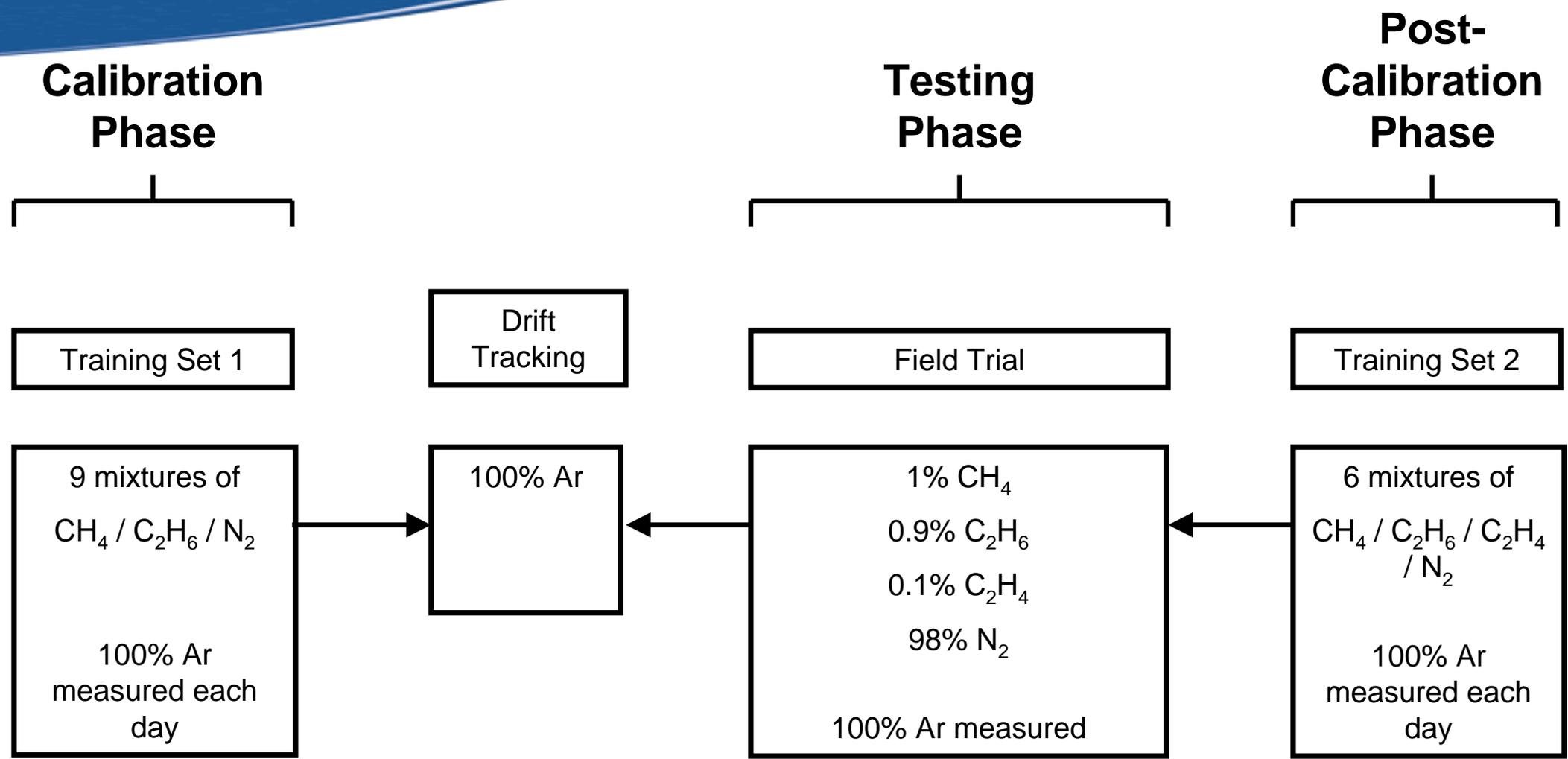
Effect of the “Unexpected” Ethylene on Quantification Accuracy



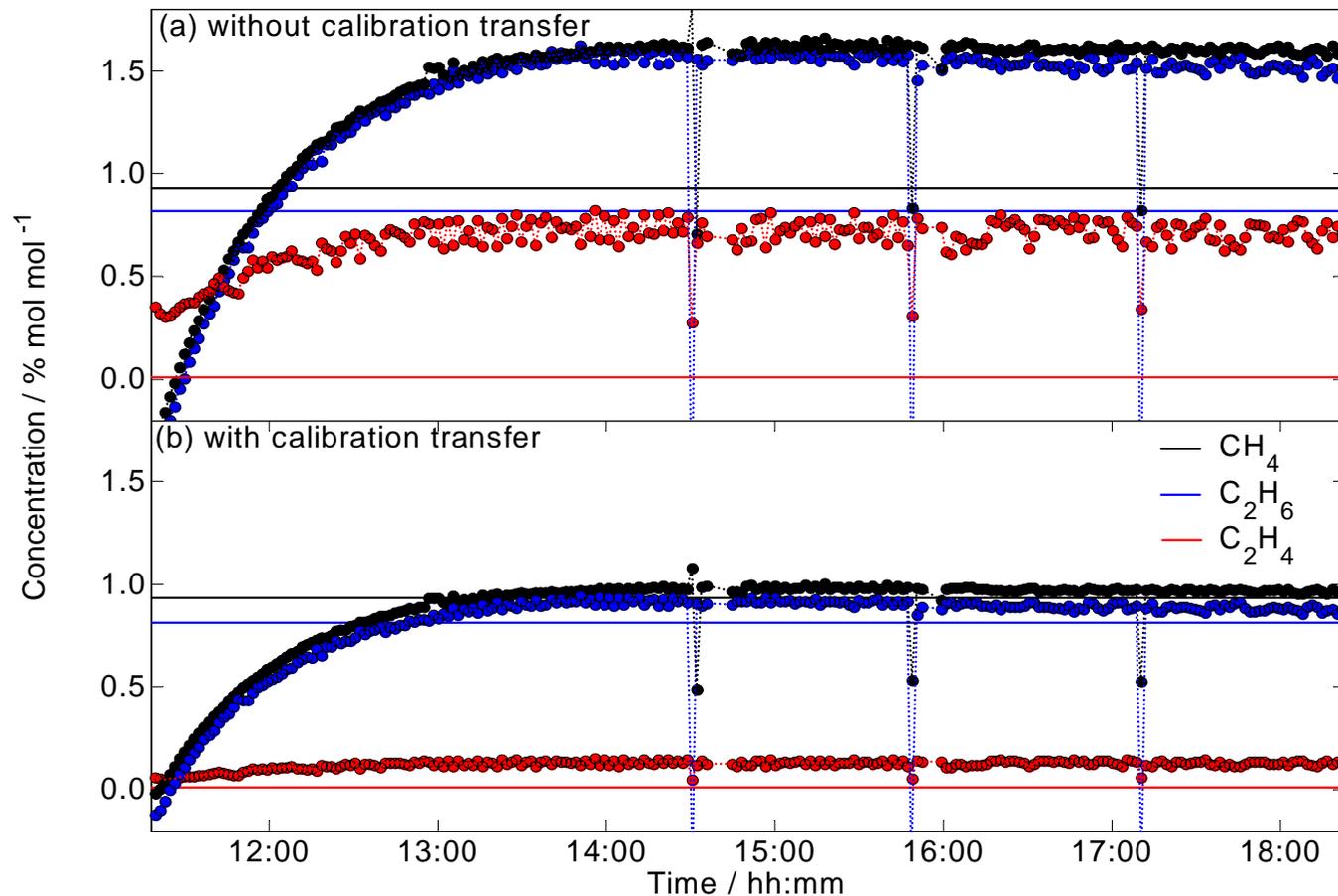
symbols = QMS determination
solid lines = actual conc.

- [CH₄] over-predicted
- [C₂H₆] markedly over-predicted due to cross-interference
- Would then inspect spectra to identify interferent
- Might then be necessary to post-calibrate to quantify/remove interferent
- Don't want to go through a complete recalibration
- Hence, desirable to measure a low number of additional mixtures including ethylene and combine training sets

Field Trial Data Set (2)



Attempting to Combine Pre- and Post-Calibrations



- Combining training sets 1 and 2 leads to decreased accuracy (a)
- This is due to drift between calibrations resulting in conflicting spectral information
- However, if correct for drift can use all pre- and post-calibration information and obtain data of much improved accuracy (b)

Conclusions

- Mass spectrometry is potentially a powerful tool for process/emissions monitoring as it is capable of detecting multiple species on-line and in real-time
- Of the various types of mass spectrometer available QMS and TOF lend themselves well to monitoring due to the availability of relatively low cost, portable instruments
- In order to realise the full multiple species capability it is often necessary to calibrate with a large number of multi-component mixtures at potentially significant cost
- However, we have seen how instrumental drift can invalidate calibrations in as little as a few weeks
 - To repeat the complete calibration is economically and practically unviable
- It has been shown that using a relatively straightforward calibration transfer strategy it is possible to significantly improve quantitative accuracy and prolong calibration lifetime

Where next?

- Can ambient air be used for calibration transfer?
- Increase number of species
- Move from stack simulator to plant
- Continue to develop more sophisticated transfer strategies
 - Thus far have experimented looking at adjusting calibration spectra based on determined I.E. on a given measurement day
 - Can Artificial Neural Networks (ANN) be applied to this type of calibration transfer problem?
- Please talk to us if you have any thoughts on mass spec. or also the NPL Stack Simulator