

# Online Mass Spectrometry - A Method for Future Emission Monitoring?

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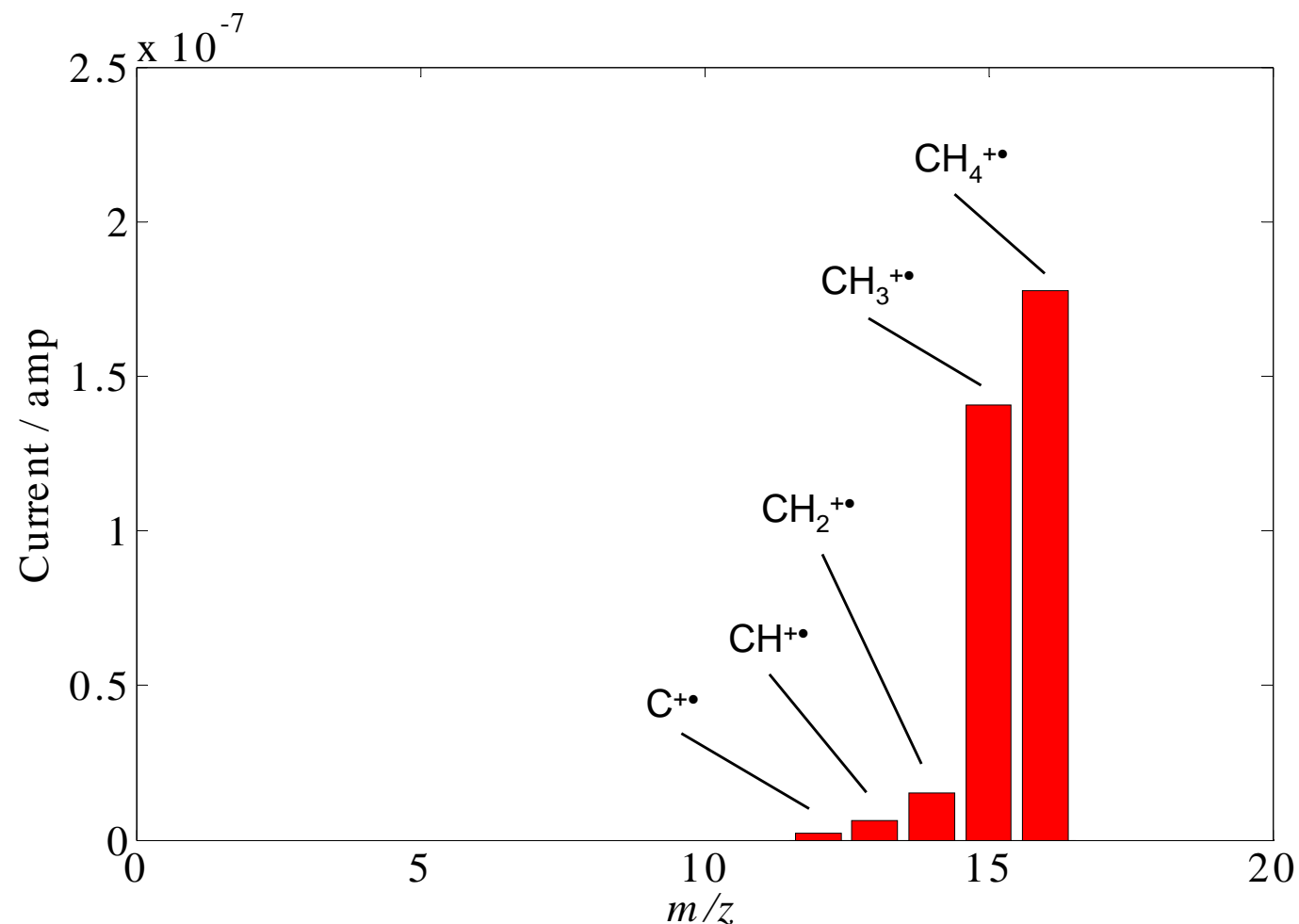


- Introduction to mass spectrometry
- Potential benefits of using QMS for process/emissions monitoring applications
- Effect of instrumental drift on quantitative analyses
- Using a Calibration Transfer Strategy to correct for the effects of drift
- Testing the strategy using NPL's Stack Simulator

- If a molecule, or atom, is bombarded with electrons it can be ionised
  - $\text{CH}_4 + \text{e}^- \rightarrow \text{CH}_4^{+\bullet} + 2\text{e}^-$
- 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 maybe 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

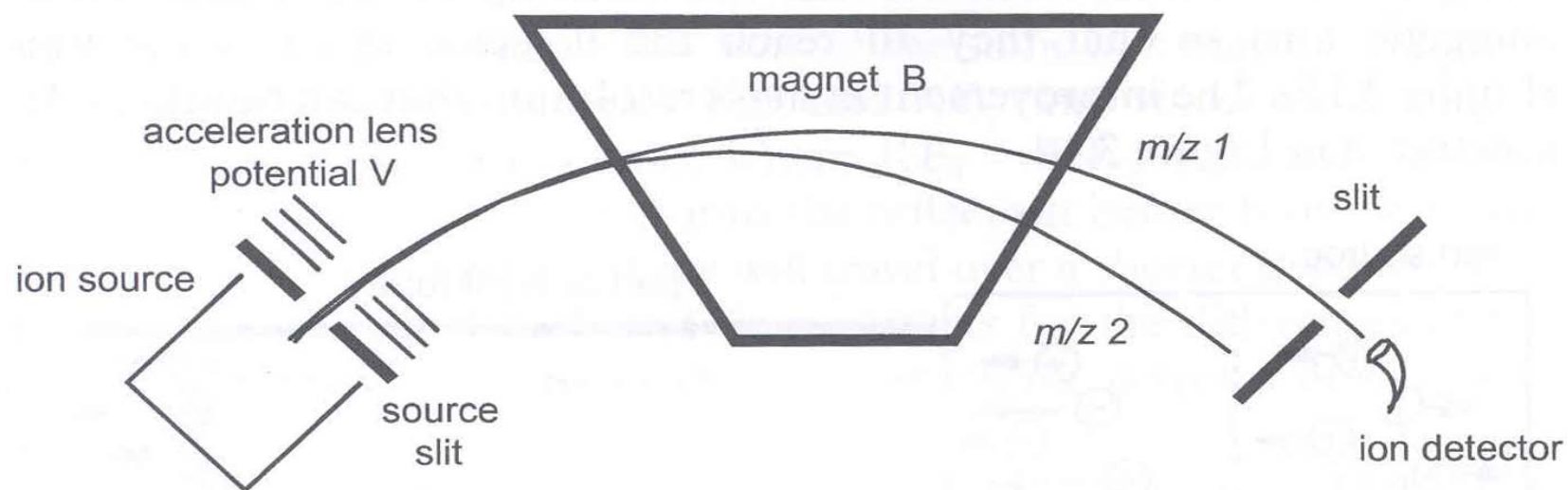
## Example Mass Spectrum of CH<sub>4</sub>

- nb.* As CH<sub>4</sub><sup>+</sup> has the same mass as the CH<sub>4</sub> from which it was produced, this is often called the parent ion

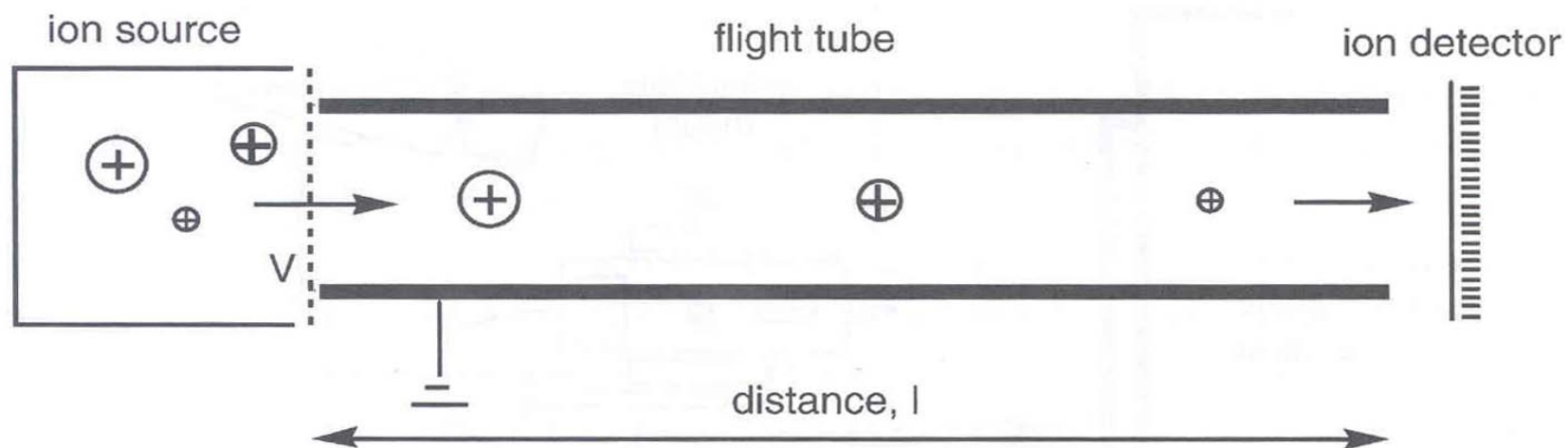


# Some Common Types of Mass Spectrometer

- Magnetic Sector

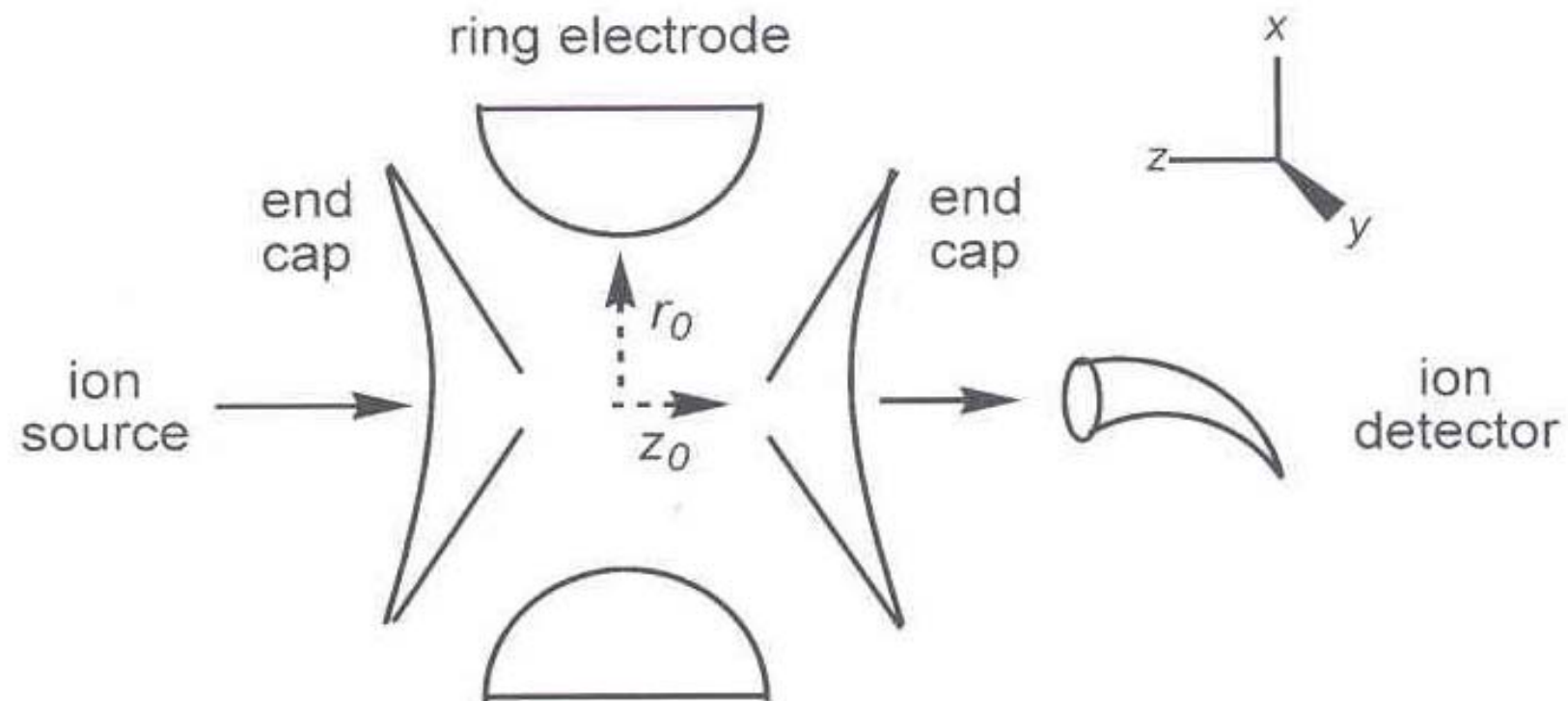


- Time of Flight (TOF)



# Some Common Types of Mass Spectrometer

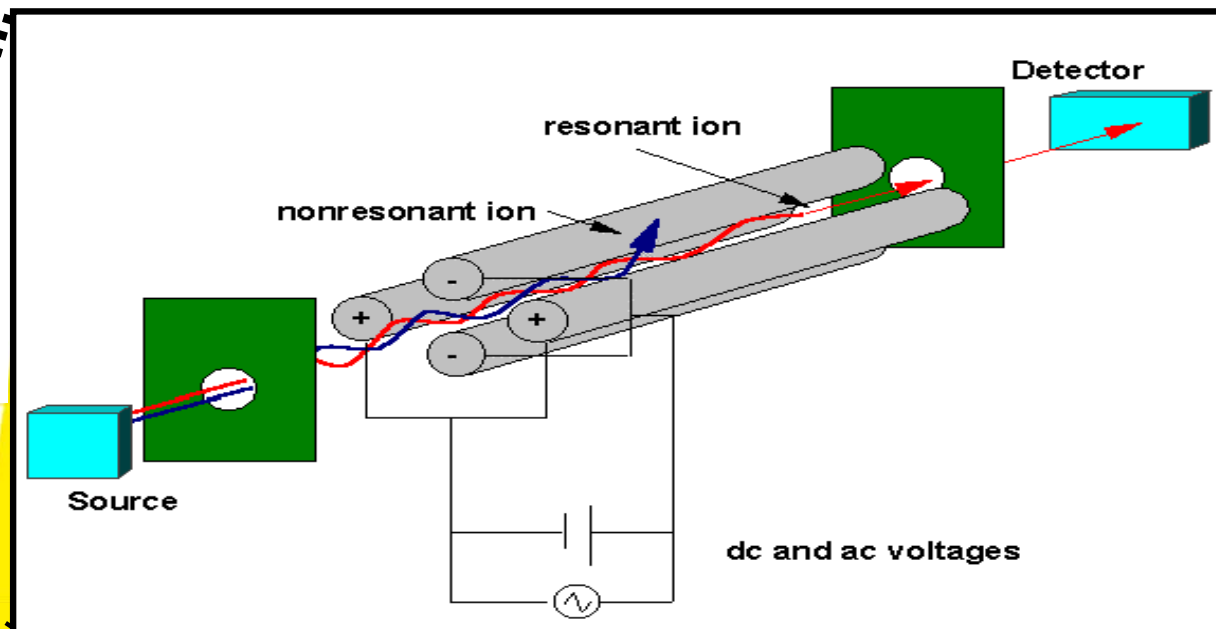
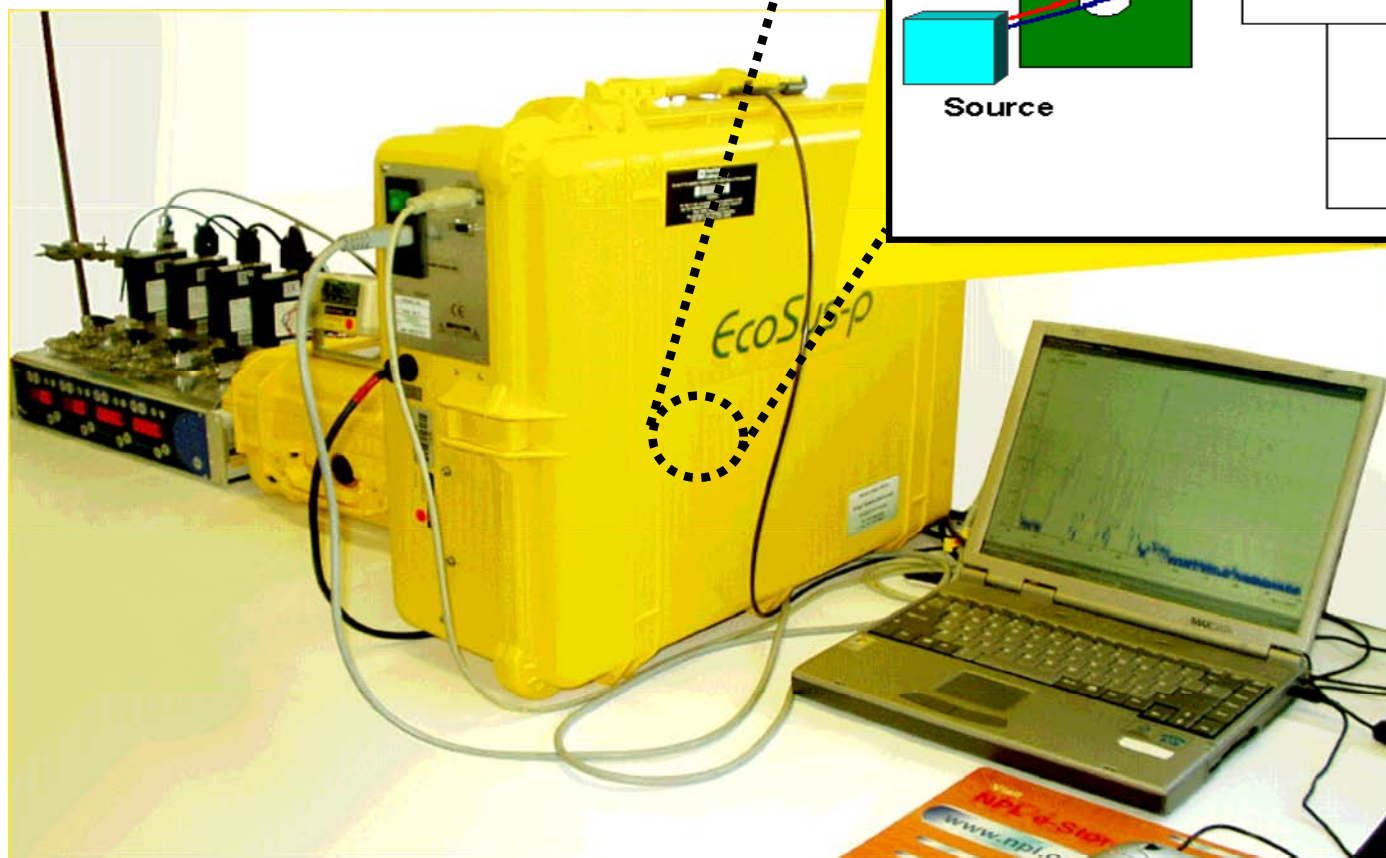
- Ion Trap (IT)





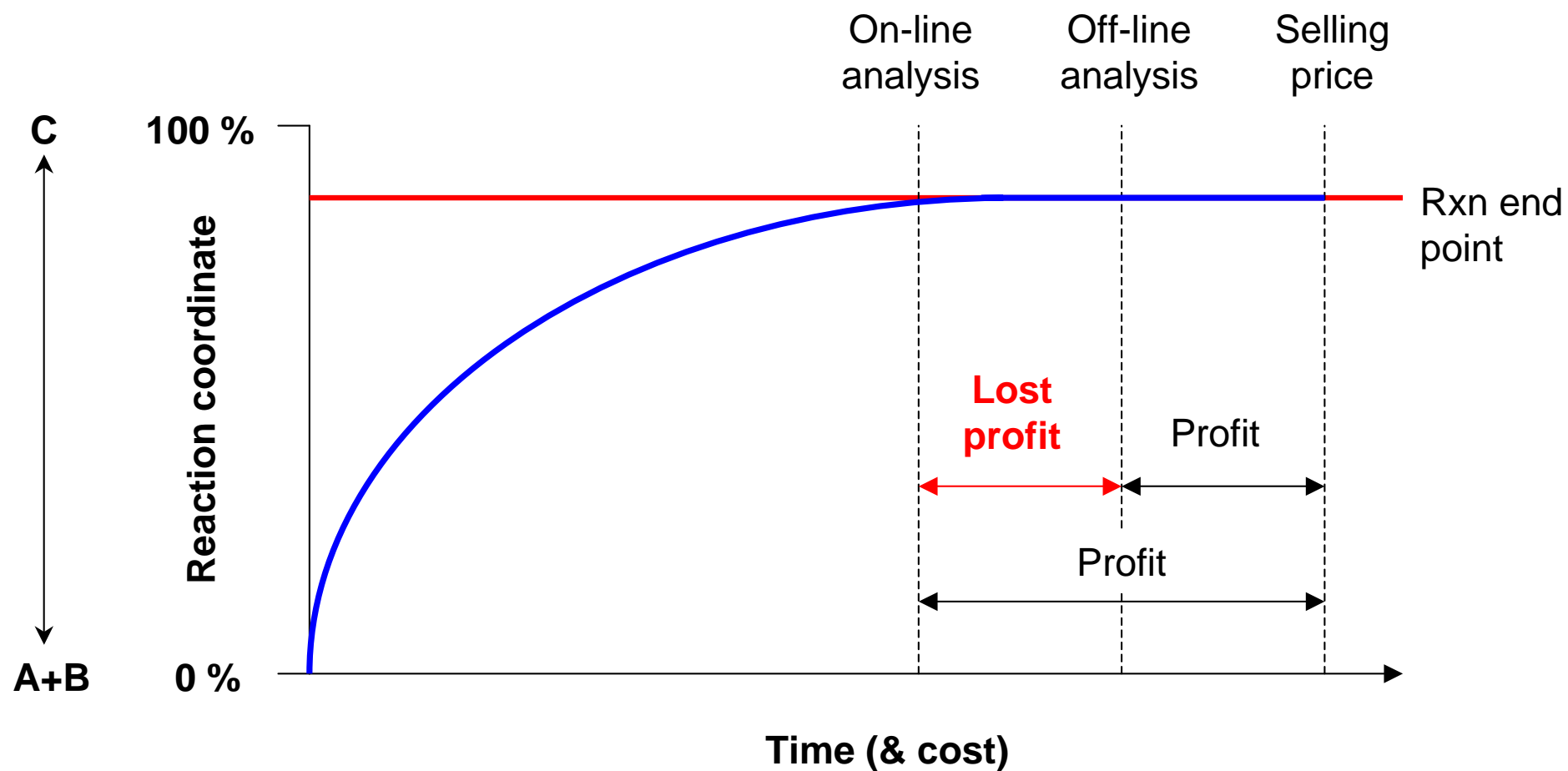
# Portable Quadrupole Mass Spectrometer (QMS)

- 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**

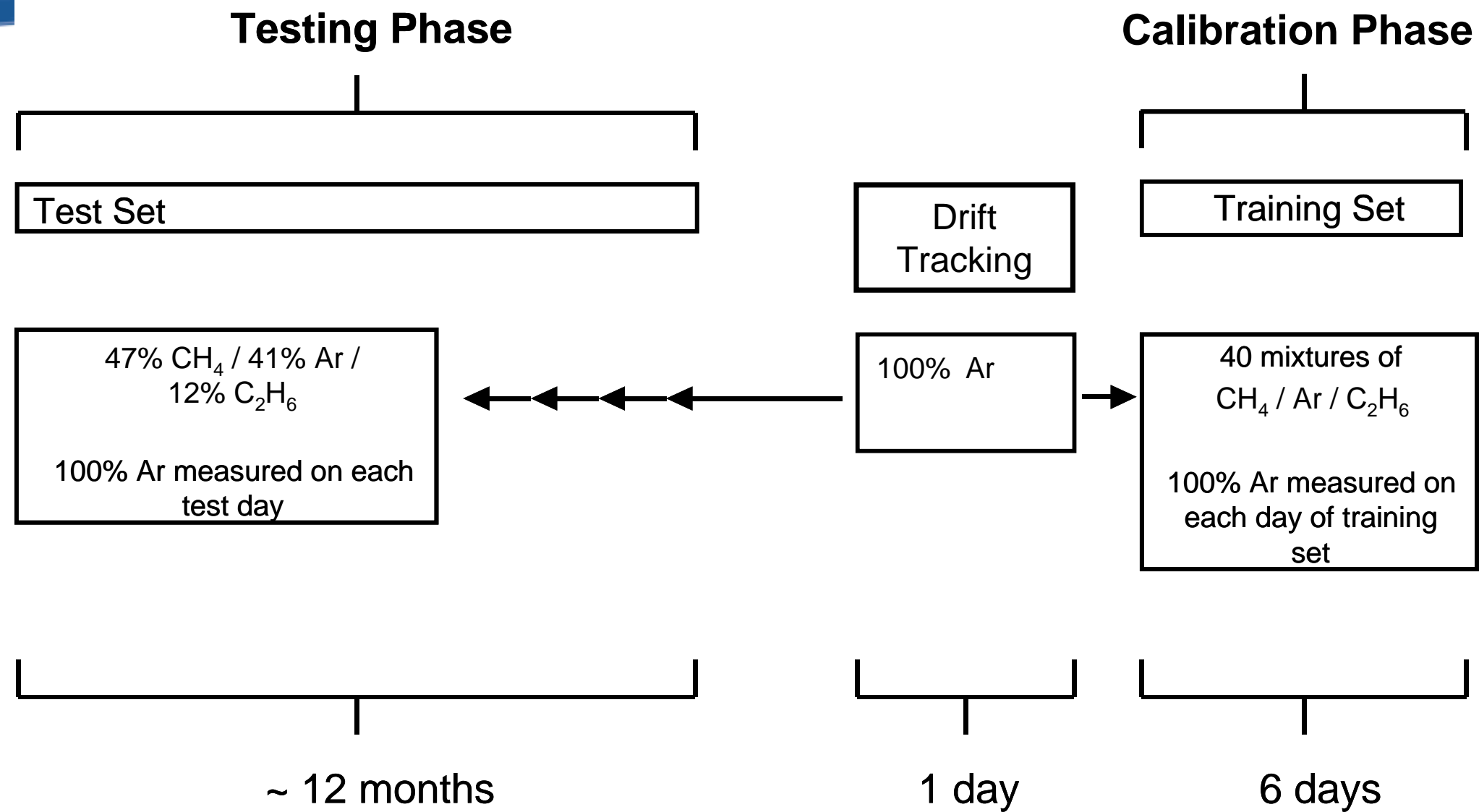
# Advantageous & Disadvantageous of Portable QMS

Advantageous	Disadvantageous
On-line, real-time monitoring	<b>Instrumental drift</b>
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

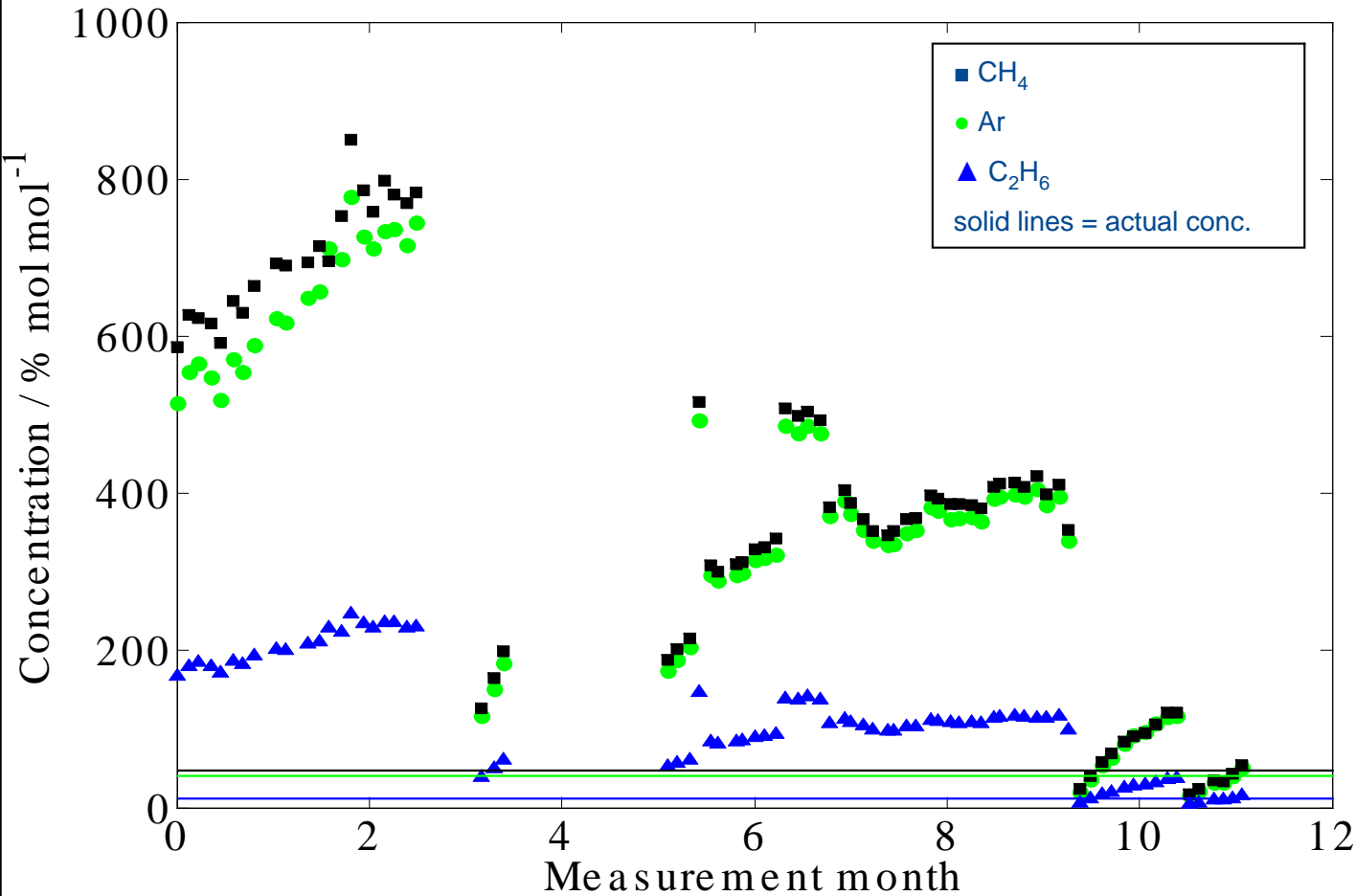
# Laboratory Dataset Schematic



# 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



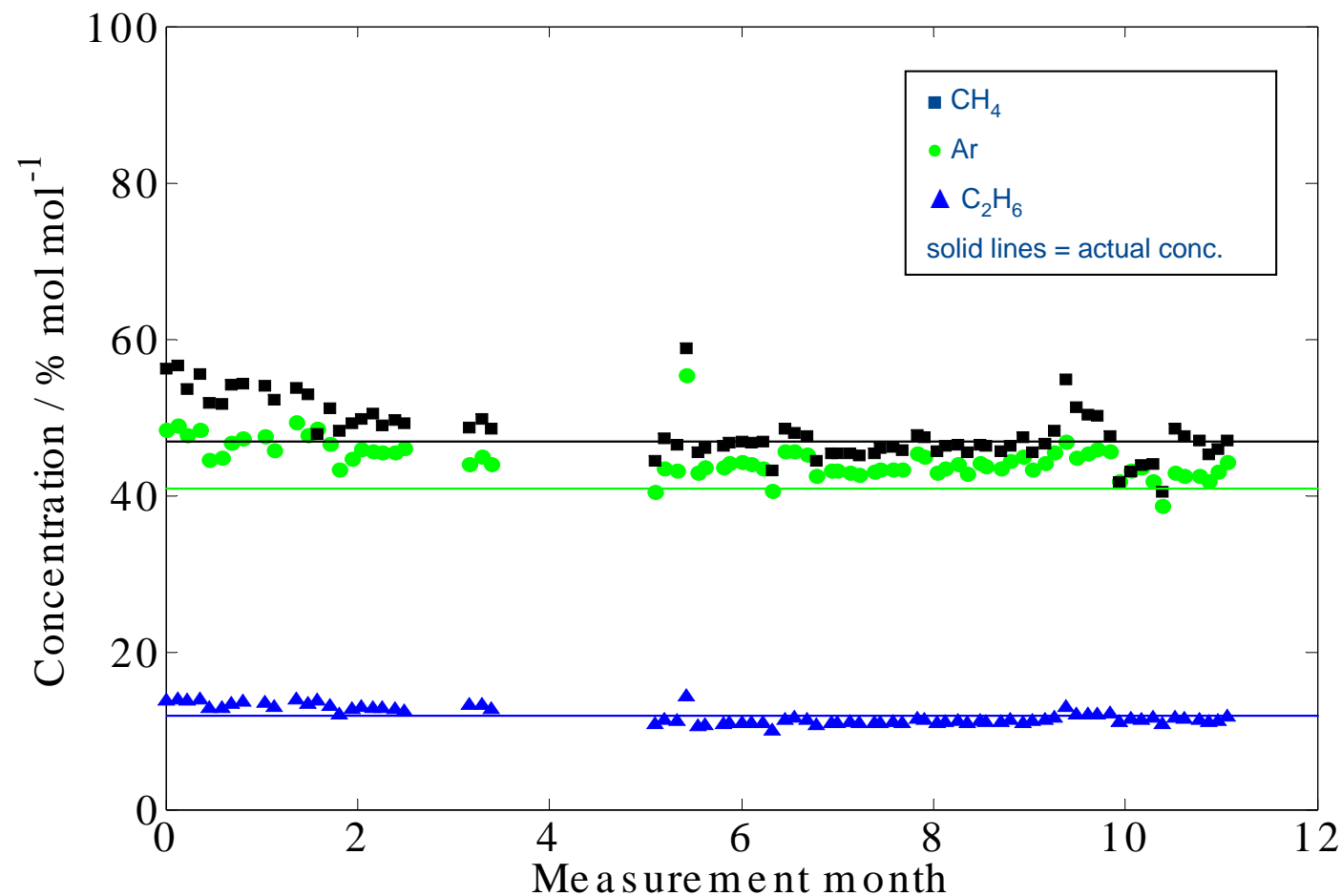
- The principle of calibration transfer is to adjust spectra to appear as though they were all recorded on the same day
- We have experimented with various approaches (e.g. adjusting spectra based on measuring change in instruments electron energy) and this is the subject of ongoing work
- However, thus 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

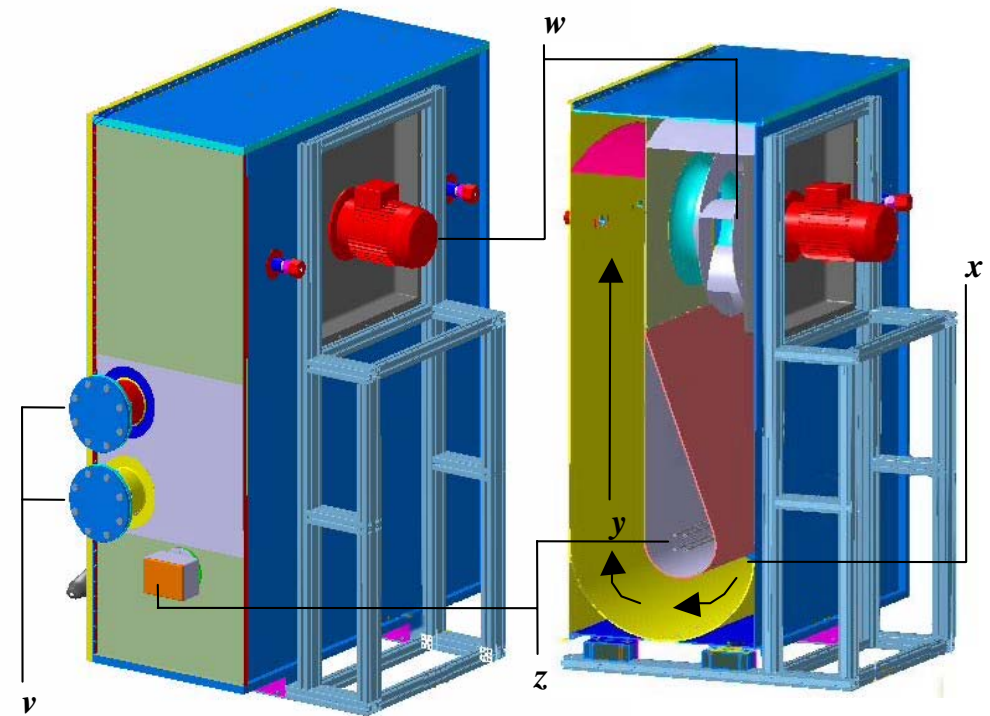
# Quantification when Employing the Calibration Transfer Strategy

- 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  $12 \text{ ms}^{-1}$  due to a centrifugal fan ( $\omega$ )
- Temperatures up to  $200 \text{ }^{\circ}\text{C}$  ( $z$ )

# Small Digression (1) - Stack Simulator

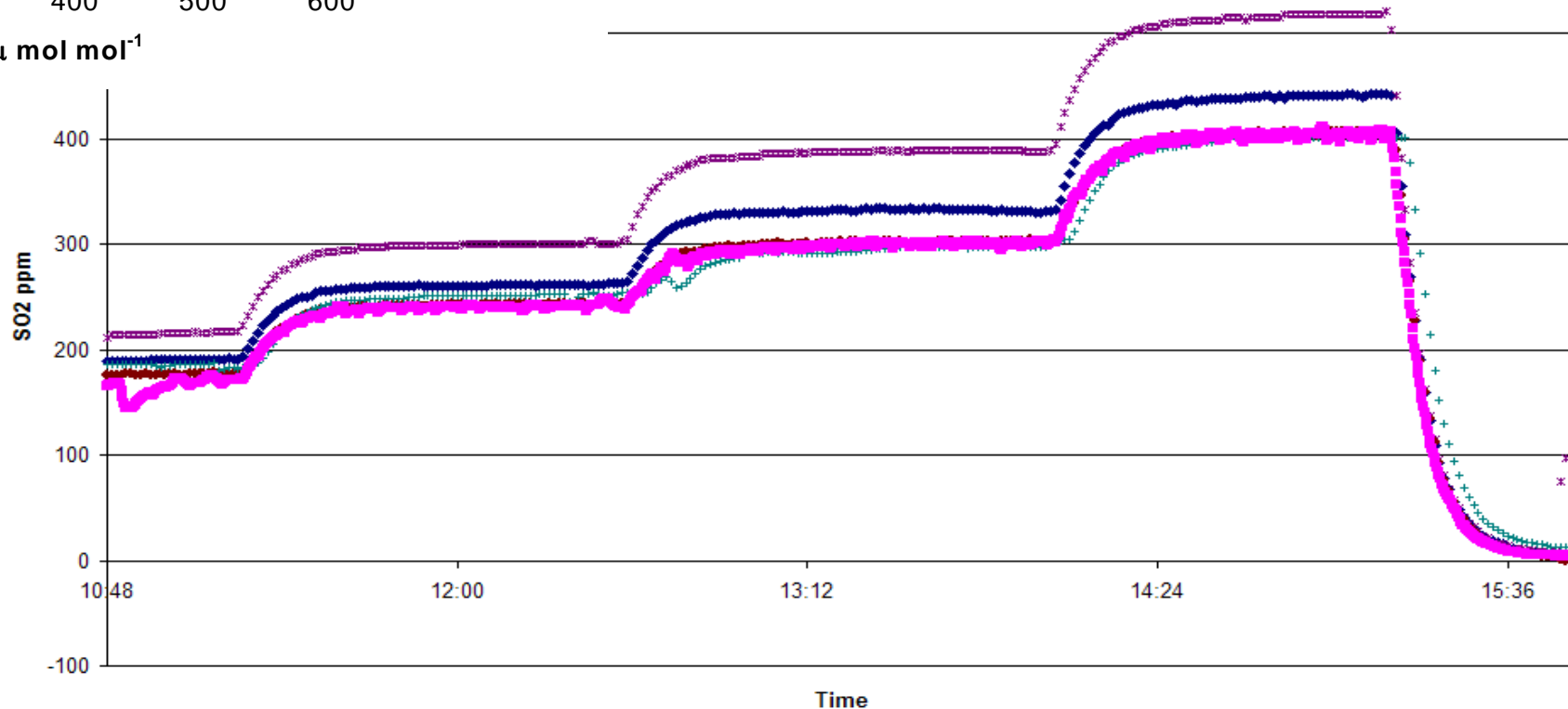
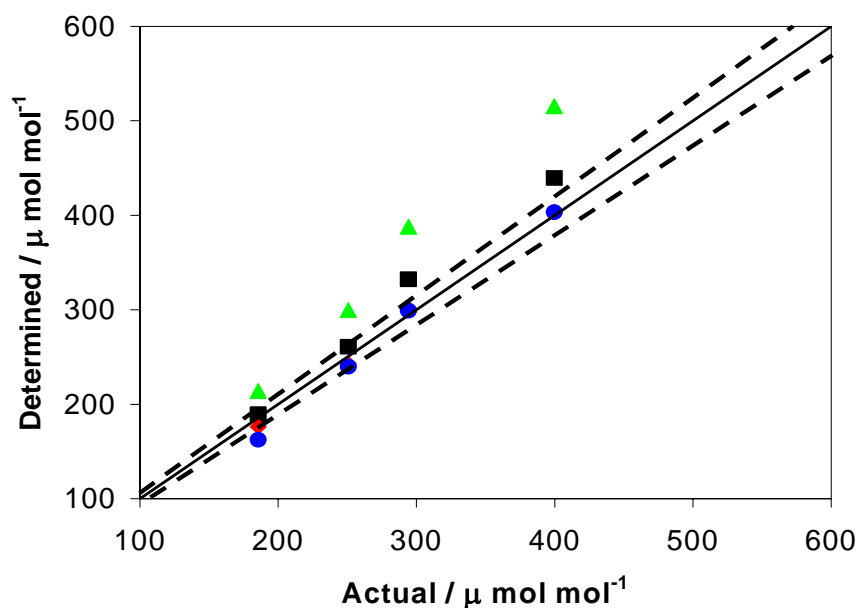
## Trial of a PT Scheme

- Four STA members anonymously took part in a trial of a PT scheme
- Tested with mixtures of
  - CO, O<sub>2</sub>, SO<sub>2</sub>, NO
  - with four step changes in concentration
- Concentrations referenced using FTIR
- Particulates next



## Small Digression (2): Results for SO<sub>2</sub>

- Company (▲) could not quantify SO<sub>2</sub> to requirements of WID
- Problem traced back to error in calibration standard
- [see Spring 2007 issue of International Environmental Technology for further info]

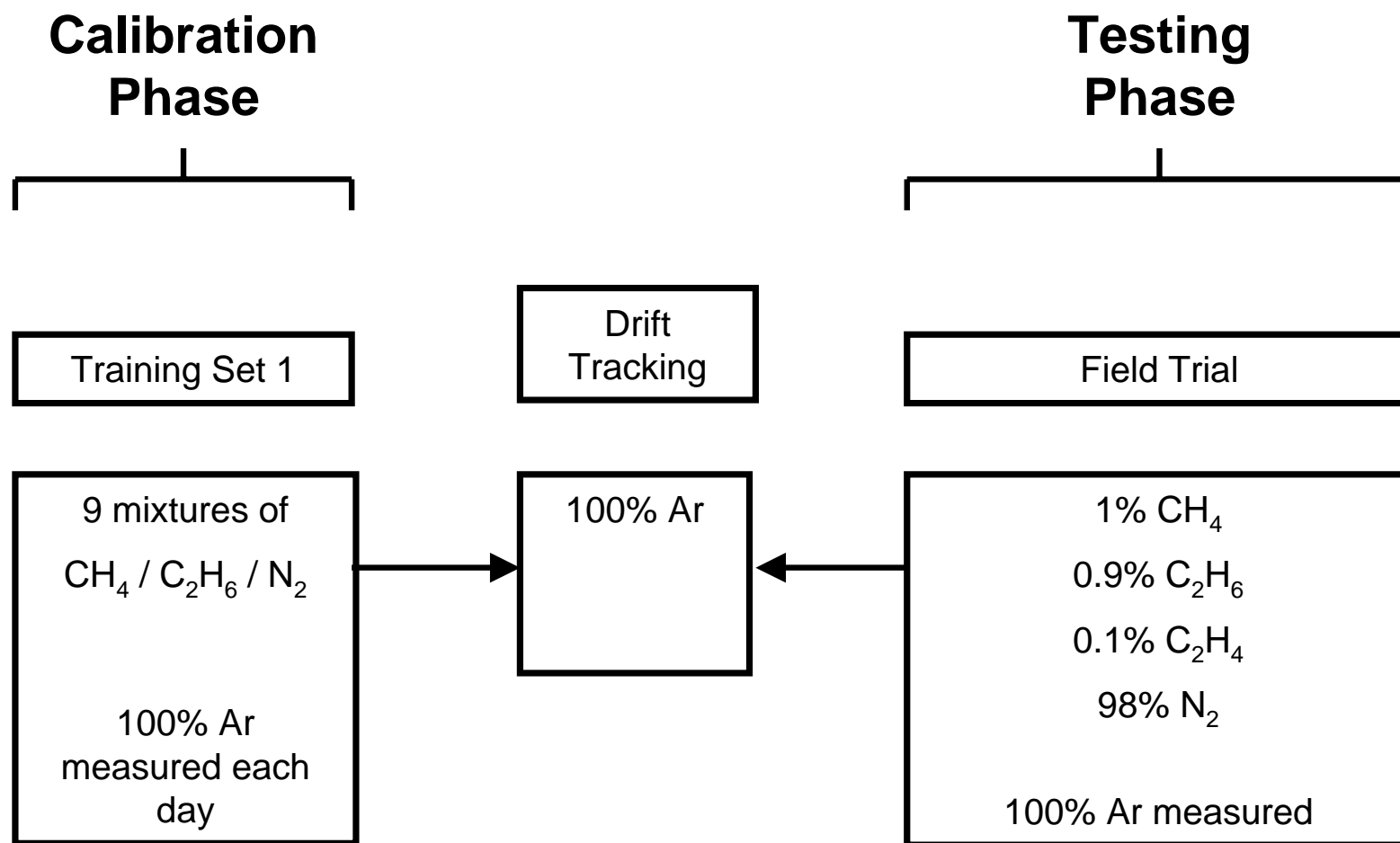




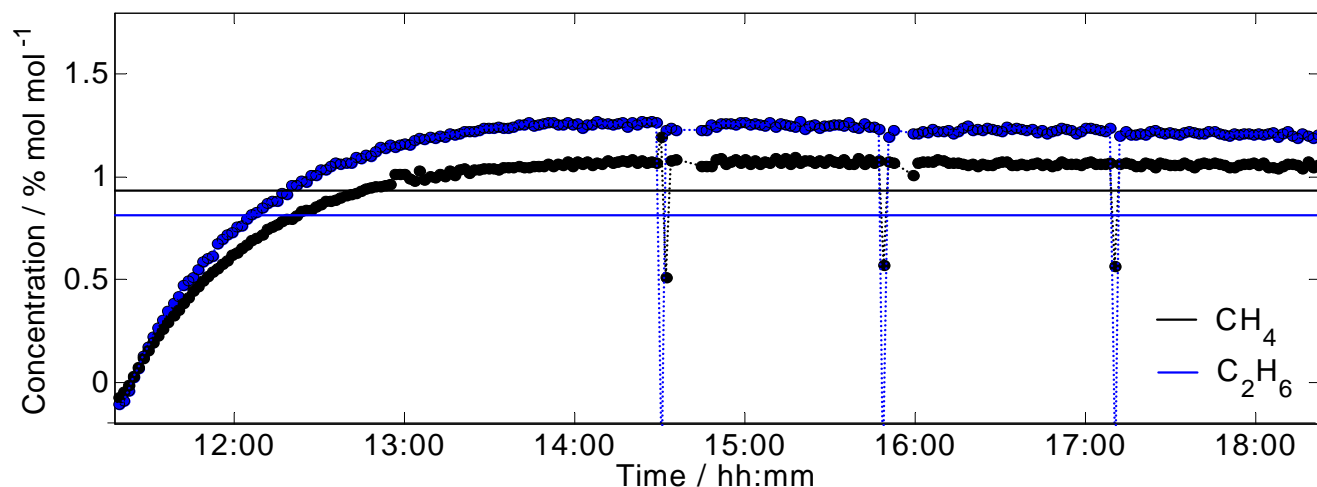
- Data set designed to
  - (a) Show the effect when a species not included in the calibration is present on the field trial
  - (b) Show the problems of trying to post calibrate for an “unexpected” species when using a multi-variate approach



# Field Trial Data Set (1)

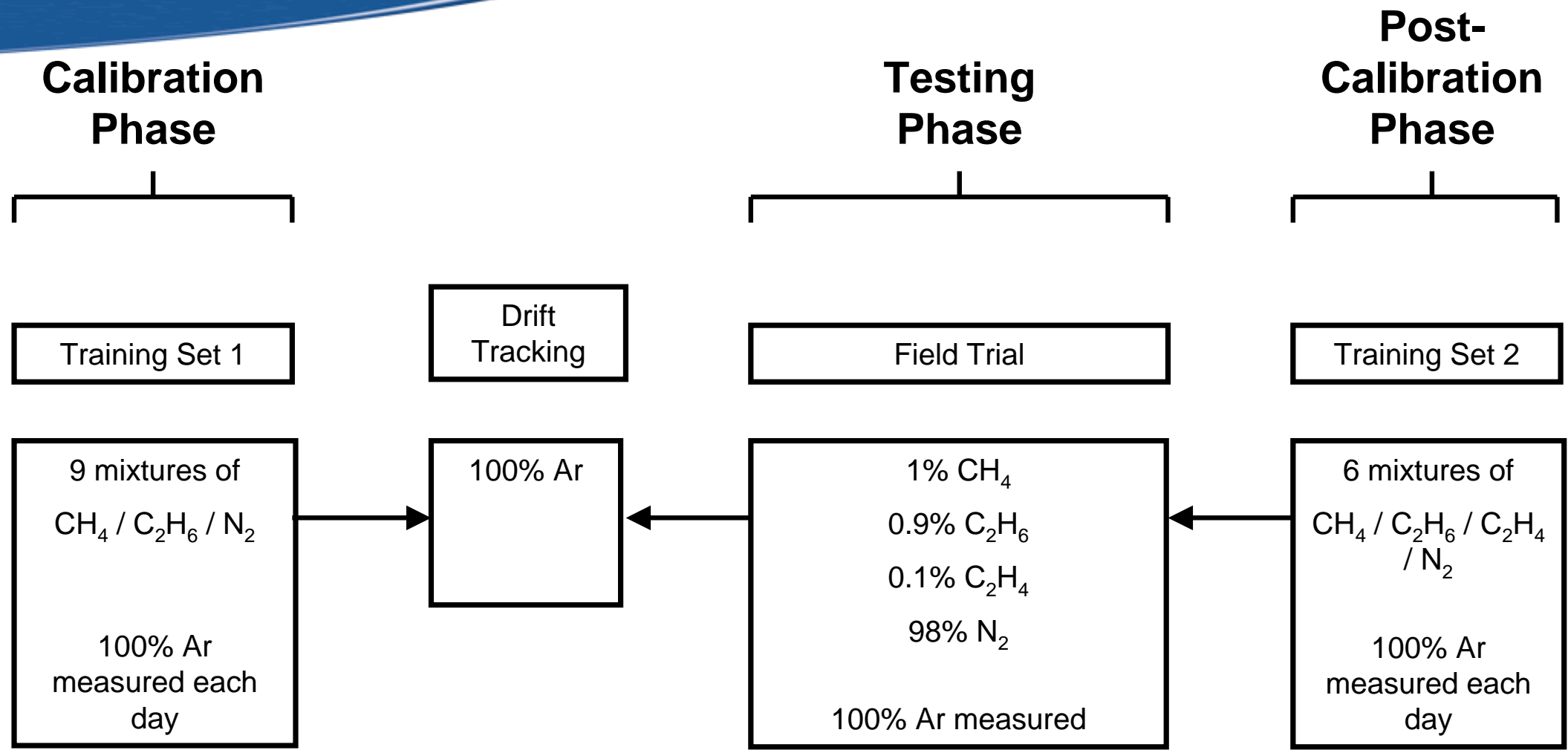


# Effect of the “Unexpected” Ethylene on Quantification Accuracy

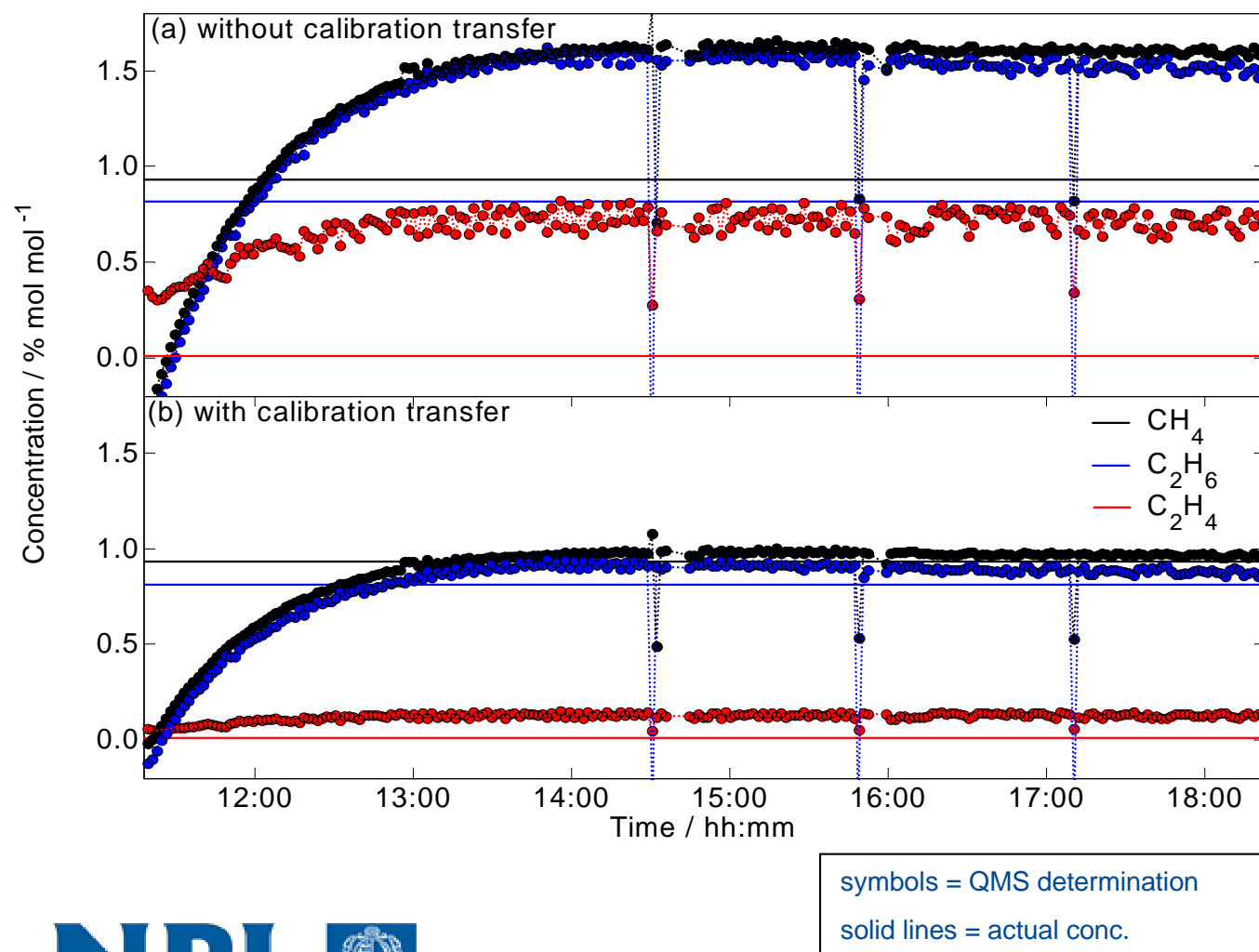


- [CH<sub>4</sub>] over-predicted
- [C<sub>2</sub>H<sub>6</sub>] markedly over-predicted due to cross-interference
- Would then inspect spectra to identify interferent
- Might then be necessary to post-calibrate to quantify/remove interferent
- Don't want to go through a complete recalibration
- Hence, 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

- 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