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# **Measurement ratification**

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  A bit of advanced stuff



## What is ratification?

- Retrospective and final calculation of measurement data set
- Establishes and uses calibration and service history
- Connects each measurement to a traceable calibration
- Ensures traceability of final measurement dataset to national metrological standards



## What is ratification?

Important point:

- QA/QC procedures do not ensure that the measurement generated by the analyser is the final and most 'accurate' measurement.
- Instead we
  - Ensure best possible functioning of the analyser
  - Collection of extensive calibration information



## Sources of information

Local Air Quality Management Guidance TG03

Minor reference in the AURN LSO manual

Minor reference in CEN Standards

- Eg EN 14211 is 91 pages and only reference to measurement processing is
- "Measured drift in the analyser's response that is less than the action criteria .... shall be corrected for in data processing and not by physical adjustment of the analyser."



Ambient measurement = SF(Analyser measurement – Zero)

Where SF = Traceable calibration gas / (Span response – zero)

Illustrated by fictional case study

- Only show work done on the service and calibration history
- Only focus on the span factor























































Simple example and only part of the process...

- Same process with zero measurements
  - Changes each span factor
- Exclude non ambient data
  - Review decisions made at validation
  - Exclude further measurements
  - Restored measurements excluded during validation
- Apply to the measurements
  - (do all this at 15 min mean resolution in practice)



Examination of final data set to

- NO2 response during incidents?
- Compare other sites?
- Compare other pollutants?















# Some more advanced stuff

- NOX, NO and NO2
  - NOX and NO done separately then look at NO2
- O3
  - Only calibrated at audit, service and repair
  - Traceablity of ESU photometers?
- PM10
  - Little calibration information
  - Filter change artefacts eg noise

More complex cylinder problems eg drift and NO oxidation



#### Some more advanced stuff When did a fault occur?

Eg fault found at 6 monthly audit but should we delete 6 months measurements?

-Can it be determined from calibration performance?

-Traced to service / repair?



#### Some more advanced stuff

Cumulative Sum (CUSUM)

Page (1954) for industrial process control

Other applications include:

-Epidemiology

-Efficacy of treatments

-Change points in air quality measurements

-Barratt et al 2006

-Carslaw et al 2006



# Some more advanced stuff -CUSUM

$$z_i = \frac{x_i - x}{\hat{\sigma}_x}$$

is the observed value at time *i*,  $\frac{x_i}{x}$ 

- is the desired process mean
- $\hat{\sigma}_{r}$ is an estimate of the standard deviation of the observed values.

These are accumulated over time to compute the CUSUM, S, at each time point *i* 

 $S_i = S_{i-1} + z_i$  where  $S_0 = 0$ 

Separate application to positive and negative deviations, with a 'slackness' factor k

$$S_{\text{Hi}} = \max[0, (z_i-k) + S_{\text{Hi-1}}]$$

 $S_{Li} = min[0, (z_i+k)+S_{Li-1}]$ 



#### Some more advanced stuff – a knotty problem at Watford

During 2005 PM<sub>10</sub> improved the roadside in Watford

-It got so good that the annual mean fell below nearby background sites!

-No maintenance and service problems

-Sustained perfect audit results



#### Some more advanced stuff – a knotty problem at Watford





#### Some more advanced stuff





#### Some more advanced stuff – a knotty problem at Watford

CUSUM identified a change at service

Through investigation by new ESU revealed an accidental entry of 6.196 instead of 3 as the TEOM offset by previous ESU

-TEOM software was corrected

-Measurements were recalculated to remove the offset error



#### Some more advanced stuff – a knotty problem at Watford – fixed!





# Some more advanced stuff

#### – a knotty problem at Watford – fixed!





#### What difference does it make? Data capture

#### 50 40 30 20 10 Change data capture 0 Kens and Chel Kens and Chel Kens and Chel H'smith and H'smith and ity o Valthe -20 -30 -40 -50 -60



#### What difference does it make? Annual mean NO2





#### What difference does it make? Hours > 105 ppb / 200 ugm3





# Summary

- What is ratification?
  - Retrospective
  - Uses calibration and service history
- How is it done
  - Fictional case study
  - A bit of advanced stuff