IMPRESS 2: WP1

Analytical laboratory comparability considerations in measuring HCl stack emissions in accordance with EN 1911

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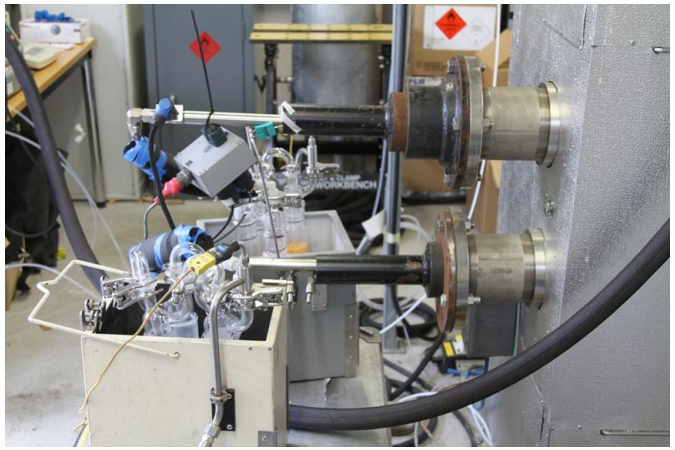
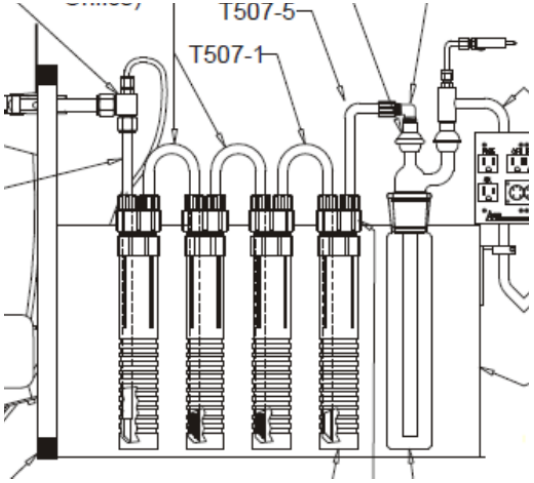
The HCl SRM

- The Standard Reference Method (SRM) for HCl is described in EN 1911
  - *'Stationary source emissions – Determination of mass concentration of gaseous chlorides expressed as HCl – Standard reference method'*
- EN 1911 is an example of a "wet chemistry" SRM
- There are both "sampling" and "analysis" elements
  - Gas is pumped out of the stack and bubbled through glass impingers containing de-H_2O. Solutions are decanted for subsequent analysis typically by ion chromatography





SRM Purpose & Emission Limits

- An SRM is used for
  - ‘Compliance monitoring’
  - Annual calibration / calibration check (EN 14181) of in-situ process plant operator’s instrumentation (AMS) that is responsible for providing continuous monitoring of emissions
  - i.e. in principle the uncertainty of all measurements is dependent on the SRM
- Whilst remaining unchanged in recent history, increasingly stringent emission limits have recently been introduced (part of the motivation for IMPRESS 2)
  - Waste Incineration Directive (2000): 10mg.m^{-3}
  - Industrial Emissions Directive (2013): 10mg.m^{-3}
  - BAT Conclusions for,
    - Non-Ferrous Metals Industries (2016): ≤1.5mg.m^{-3}
    - Large Combustion Plant (2017): 3-12mg.m^{-3}
    - Waste Incineration (2019): 2-6mg.m^{-3}

Aim of Comparison

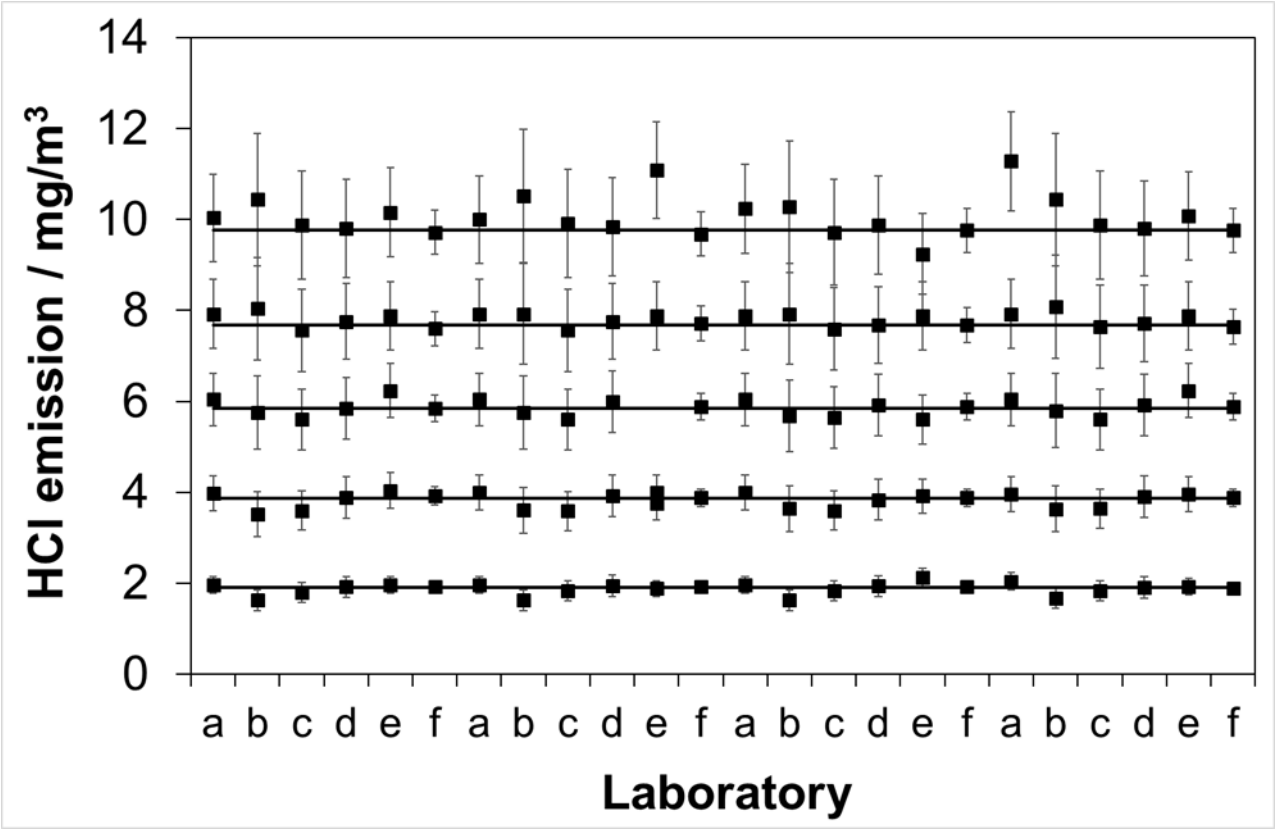
- Aim of the work was to focus on the analysis (quantitation) element of EN 1911
- Q: Is deviation across analytical laboratories significantly less than the required measurement uncertainty?
  - Deviation of individual laboratory from refence important
  - As if from laboratory to laboratory, as process plant operators can change provider

Experimental

- ILC was blind
- ‘Synthetic’ and ‘Real’ samples were prepared
- Synthetic:
  - Prepared by dissolving NaCl in de-H_2O
  - Emission equivalent concentrations of 1.9, 3.9, 5.9, 7.7 & 9.8 $mg.m^{-3}$
  - Each solution split 6-fold and despatched to 6 ISO/IEC 17025 laboratories accredited for chloride analysis in accordance with EN 1911

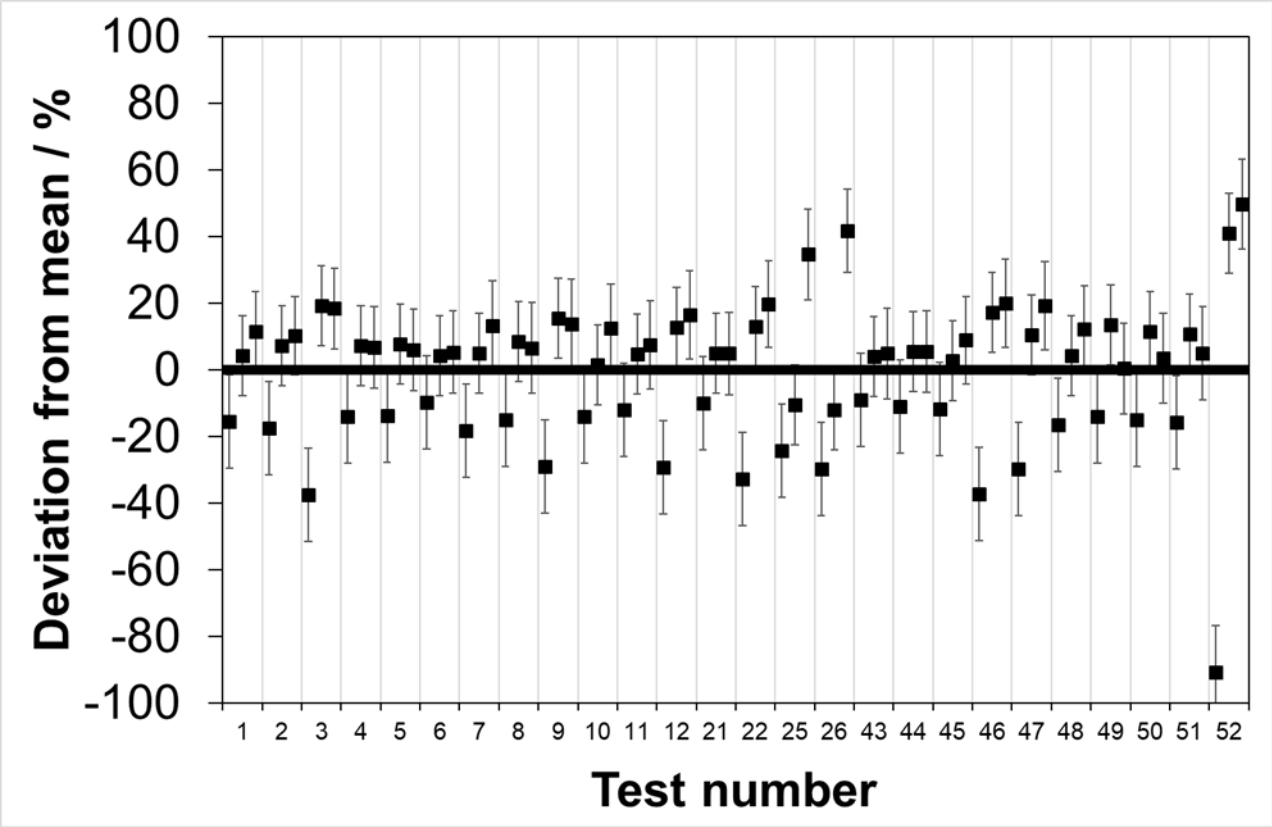
- Real:
  - Using the NPL Stack Simulator Facility 46 real emission matrices (containing representative concentrations of SO_2, CO, NO, H_2O, CO_2, O_2, CH_4, VOCs) were generated
    - NPL hold ISO 17043 accreditation for proficiency testing using this facility
  - EN 1911 samplings were carried out by NPL staff certified to MCERTS level 2 under the Environment Agency’s Personal Competency Standard
  - Impinger solutions were split 3-fold and despatched to 3 of the 6 laboratories

Synthetic Quantifications 0-10mg.m^{-3} Range



- 7 out of 120 (5.8%) deviate from the reference in excess of the laboratory's stated *k*=2 uncertainty
- Commensurate with an expanded uncertainty. i.e. ~5% of measurements expected to deviate beyond uncertainty

Real Quantifications 0-10mg.m^{-3} Range



- 33 out of 78 (42.3%) deviate in excess of the laboratory's stated *k*=2 uncertainty
- A significant contract to synthetic results
- Evidences that quantifications impacted by real sample matrix

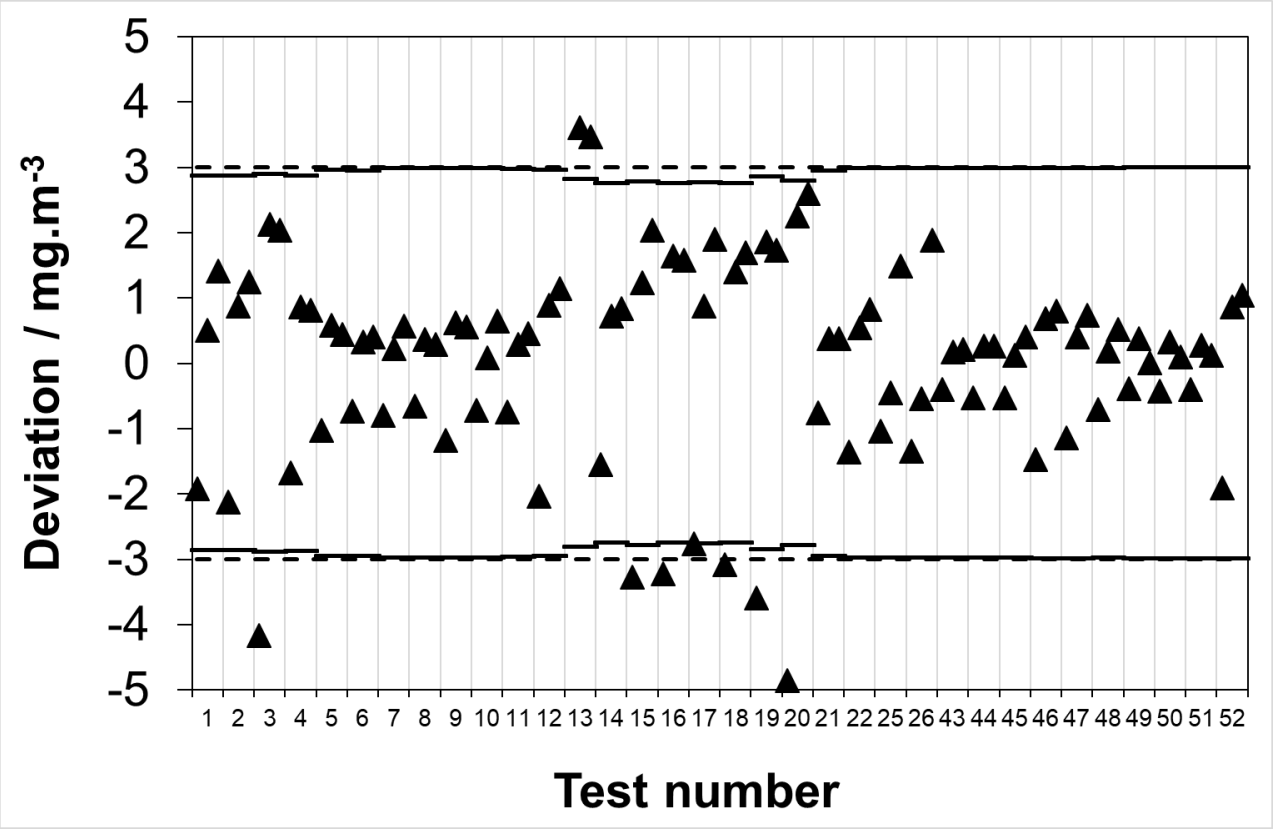
- Proficiency testing based on synthetic samples may be providing an optimistic view of what uncertainty can routinely be achieved for the quantitation element of EN 1911
- Laboratories may be underestimating their uncertainties

Global Uncertainty Requirements

- An analytical laboratory has to estimate their uncertainties as part of achieving ISO/IEC 17025 accreditation
- But, for the overall measurement method (sampling + quantitation) described in EN 1911 there is an uncertainty requirement
  - ≤30% of the emission limit (at *k*=2)
- IED emission limit = 10mg.m^{-3}
  - Therefore, absolute uncertainty requirement is ±3mg.m^{-3}
- But, must make some allowance for sampling uncertainty
  - If 7.2% of measured value is taken as a representative sampling uncertainty
    - [nb. this is probably tending towards the optimistic]
- Then, the portion of the required uncertainty left for the quantitative step is found from

$$\sqrt{U_{req}^2 - (0.72.measued\ value)^2}$$

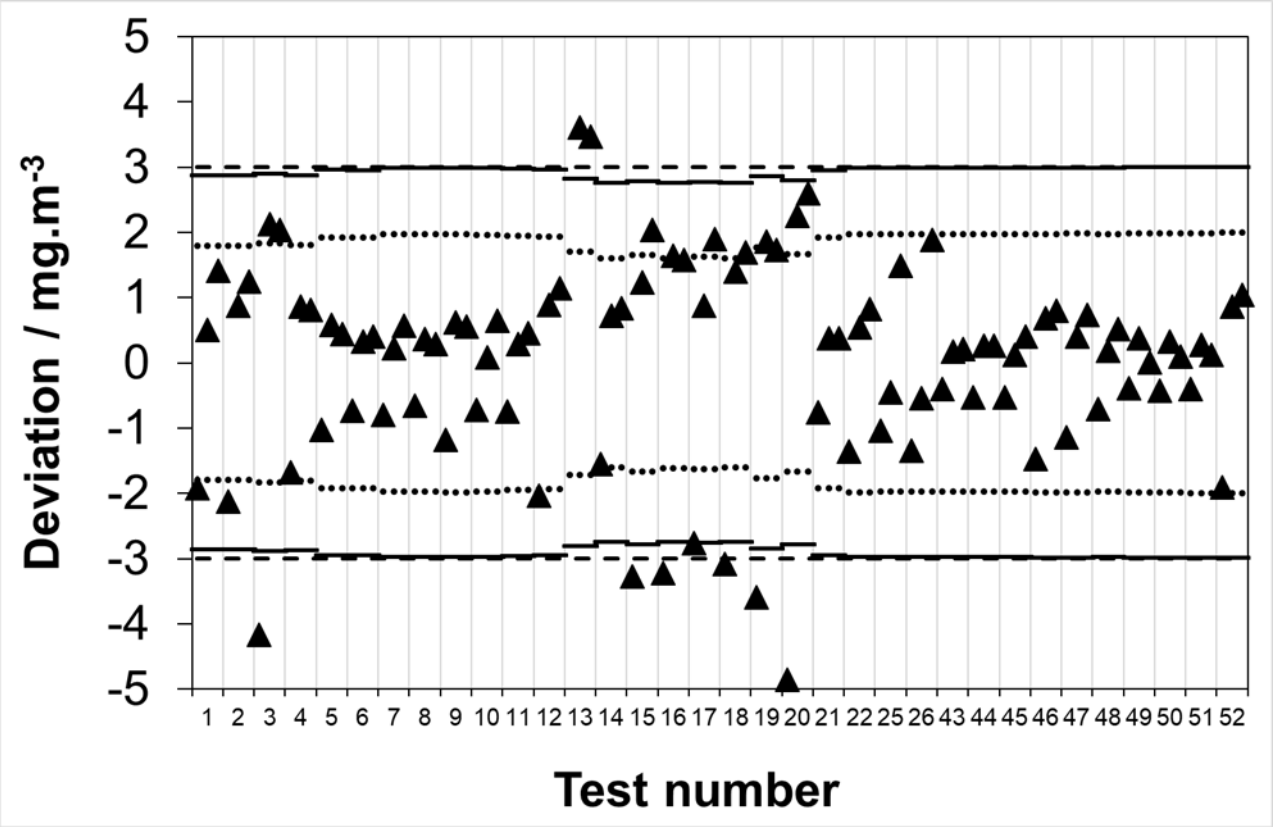
Returned Results 0-15mg.m^{-3} Range



- 10 out of 102 (9.8%) deviate in excess of the required uncertainty
- But, national requirements for EN14181 calibration
- e.g. EA in England 20% of emission limit

- (---) = 30% of emission limit (10mg.m^{-3})
- (—) = 30% of emission limit (10mg.m^{-3}) less 7.2% of value sampling uncertainty

Returned Results 0-15mg.m^{-3} Range



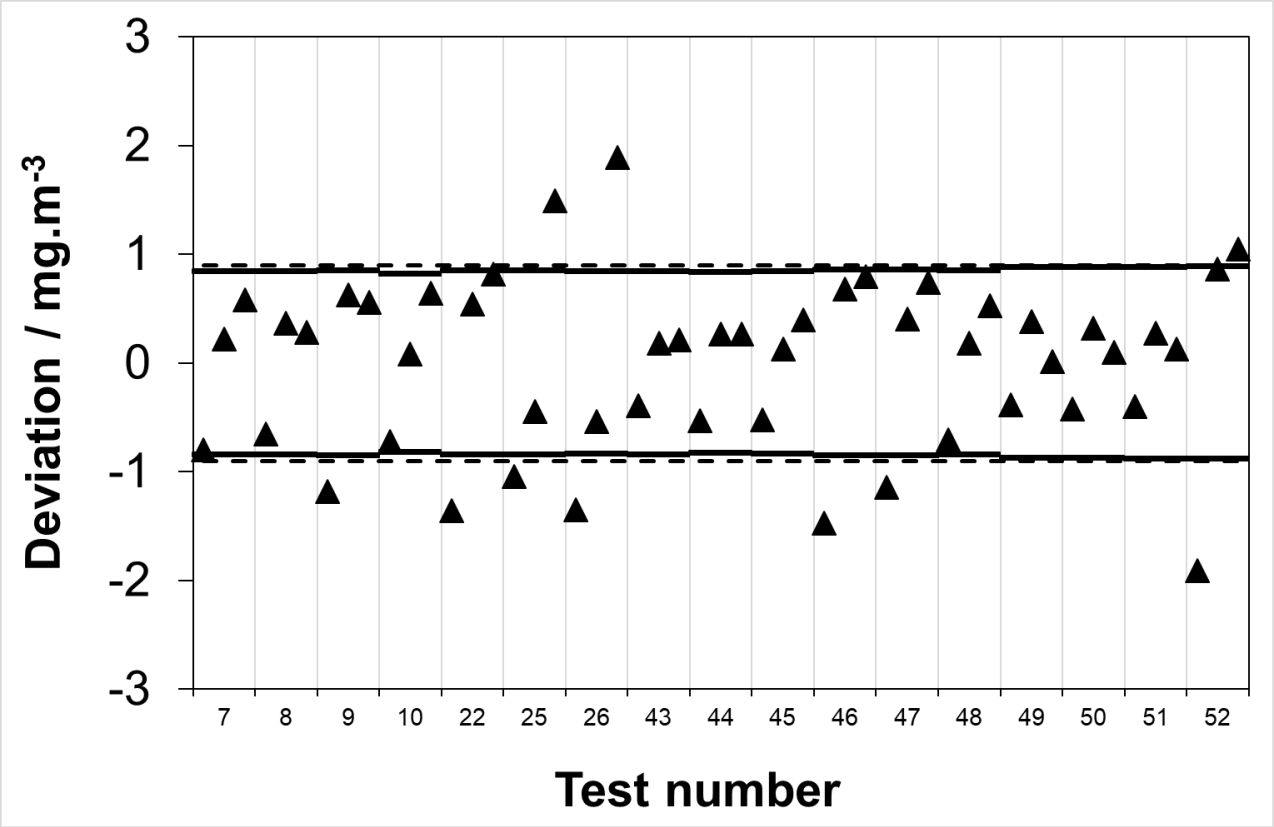
- 10 out of 102 (9.8%) deviate in excess of the required uncertainty
- But, national requirements for EN14181 calibration
- e.g. EA in England 20% of emission limit
- Now 22 out of 102 (21.6%) deviate in excess of the uncertainty

- (**---**) = 30% of emission limit (10mg.m^{-3})
- (**—**) = 30% of emission limit (10mg.m^{-3}) less 7.2% of value sampling uncertainty
- (**…**) = 20% of emission limit (10mg.m^{-3}) less 7.2% of value sampling uncertainty

Increasingly Stringent Emission Limits

- Lastly, as mentioned before emission limits have become increasingly stringent in recent legislation
  - BAT Conclusions for,
    - Non-Ferrous Metals Industries (2016): $\leq$1.5mg.m^{-3}
    - Large Combustion Plant (2017): 3-12mg.m^{-3}
    - Waste Incineration (2019): 2-6mg.m^{-3}
- Taking an emission limit of 3mg.m^{-3}
- The legislative defined measurement range is then 1.5 x emission limit, i.e. we extract data from 0-4.5mg.m^{-3}
- Then this can give some indication of the ability to enforce the new legislation

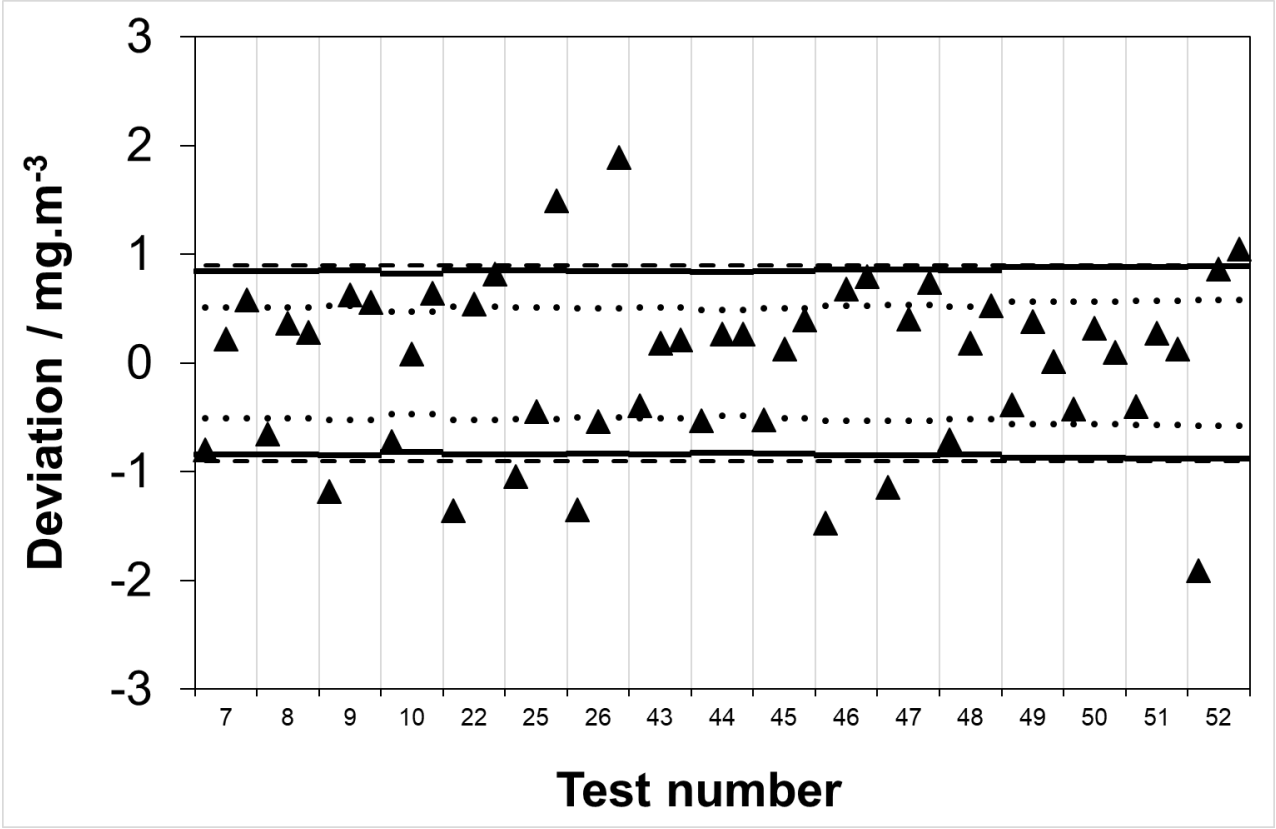
Returned Results 0-4.5mg.m^{-3} Range



- 10 out of 51 (19.6%) deviate in excess of the EN 1911 required uncertainty

- (---) = 30% of emission limit (3mg.m^{-3})
- (—) = 30% of emission limit (3mg.m^{-3}) less 7.2% of value sampling uncertainty

Returned Results 0-4.5mg.m^{-3} Range



- 10 out of 51 (19.6%) deviate in excess of the EN 1911 required uncertainty
- 28 out of 51 (54.9%) deviate in excess of the EA uncertainty

- (**---**) = 30% of emission limit (3mg.m^{-3})
- (**—**) = 30% of emission limit (3mg.m^{-3}) less 7.2% of value sampling uncertainty
- (**…**) = 20% of emission limit (3mg.m^{-3}) less 7.2% of value sampling uncertainty

Conclusions

- Proficiency testing schemes based on synthetic samples may underestimate quantitative performance
- The data some questions about the capability to not only enforce BAT Conclusions emission limits but also those from the IED
- EN 1911 provides guidance for sampling uncertainty sources and stipulated sub-requirements
  - e.g. volume of absorption solution (≤1.0%), volume of gas extracted from the stack (≤2.0%), temperature (≤2.5K), pressure (≤1.0%), sample line leaks (≤2.5%)
- For analysis EN 1911 only requires that a repeatability of ≤2.5% is demonstrated
- EN 1911 should be revised to stipulate a required uncertainty for analysis, and also provide guidance on potential analytical uncertainty sources and where appropriate set sub-requirements similar to sampling