Atmosphere Monitoring – Assessing functional limits of detection

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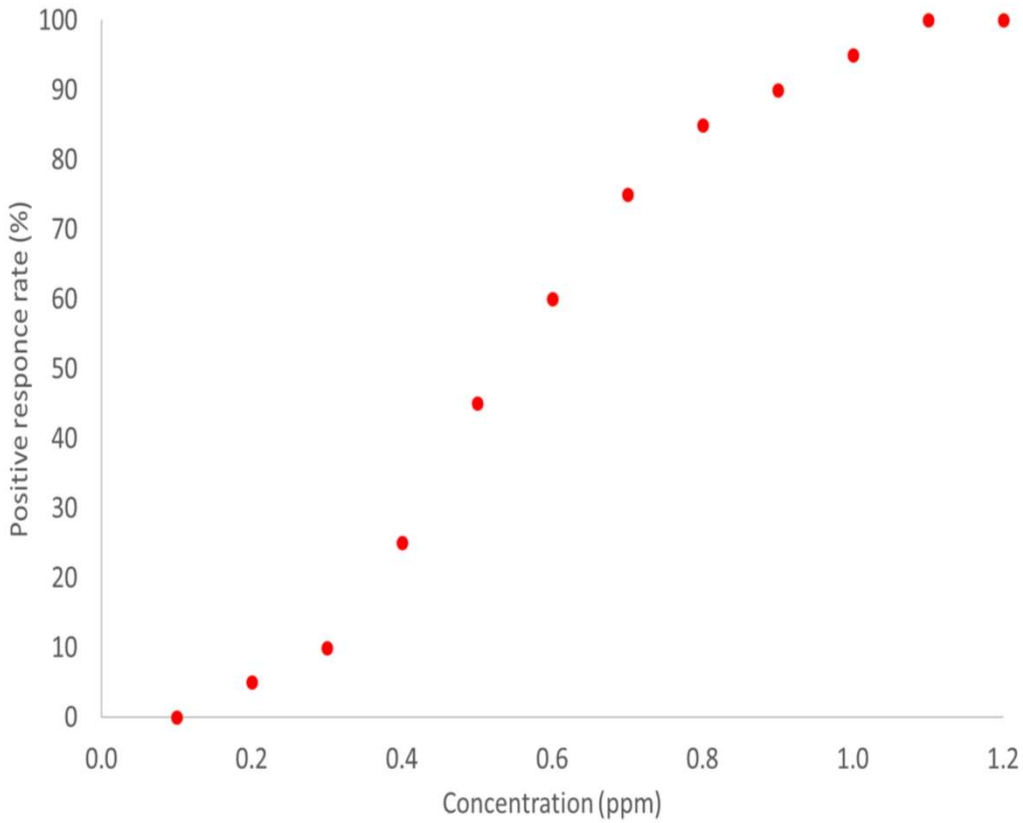

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Methods for determining lower operating limits of measuring systems

- Generally in Europe, direct reading toxic gas monitors are validated EN 45544:2015
  - This defines Lower Limit of Measurement (U_{zero}) = '*smallest value of the measured quantity within the measuring range'*
- Laboratories performing retrospective analysis are typically working to in-house validation procedure
  - Typically based on Eurachem guide '*The Fitness for Purpose of Analytical Methods*' second edition which defines
    - The Limit of Detection (LoD) = lowest level of an analyte that can be detected, with sufficient confidence, within the sample matrix
    - The Limit of Quantification (LoQ) = lowest level of an analyte that can be quantified, with sufficient confidence, within the sample matrix

Calculation of U_{zero} According to EN 45544:2015

- $ur_{zero} = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})}{n-1}}$
- $unr_{zero} = \sqrt{\left(\frac{\bar{x}}{\sqrt{3}}\right)^2 + \left(\frac{x_{res}}{2 \times \sqrt{3}}\right)^2}$
- $u_{zero} = \sqrt{({ur_{zero}}^2 + {unr_{zero}}^2)}$
- $U_{zero} = 2 \times u_{zero}$

Where:
ur_{zero} = Random element of zero uncertainty
x_i = Zero measurement
$\bar{x}$ = Mean of repeated zero measurements
unr_{zero} = Non − random element of zero uncertainty
x_{res} = Resolution of the indicating device
u_{zero} = Total zero uncertainty
U_{zero} = Lower limit of measurement

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Calculation of s_0 and s_0' according the Eurachem guide

- $s_0 = \sqrt{\sum_{i=1}^{m} \frac{(z_i - \bar{z})}{m-1}}$
- when readings are not blank corrected
- $s_0' = \frac{s_0}{\sqrt{r}}$
- or when readings are blank corrected
- $s_0' = \frac{s_0}{\sqrt{\frac{1}{r} + \frac{1}{r_b}}}$
- For a direct reading instrument this simplifies to
- $s_0' = \frac{s_0}{\sqrt{1}} = s_0$
- LoD = 3 x s_0' and LoQ = 10 x s_0'

Where:
s_0 = Estimated standard deviation of a reading at or near zero concentration
z_i = Near zero measurements
$\bar{z}$ = Mean of the repeated near zero measurement
m = Number of readings taken
r = Number of replicate readings averaged to produce a final result
r_b = Number of blank replicate readings averaged to produce a final result
s_0' = Standard deviation used for calculating LoD and LoQ

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Comparison of U_{zero} and s_0'

- $ur_{zero} = \sqrt{\sum_{i=1}^{n} \frac{(x_i - \bar{x})}{n-1}}$, and $s_0' = \sqrt{\sum_{i=1}^{m} \frac{(z_i - \bar{z})}{m-1}}$
  - are interchangeable and calculate the random element of the uncertainty
  - ur_{zero} is calculated on zero readings
  - s_0' can be calculated on zero or near zero readings

- $\mathrm{unr}_{\mathrm{zero}}$ addresses non-random uncertainty

- EN 45544:2015 uses a smaller coverage factor than Eurachem method
  - U_{zero} is 2
  - LoD is 3
  - LoQ is 10

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Selection of coverage factors

- EN 45544:2015 does not explain how the coverage factor for U_{zero} value was derived

- Eurachem Guide explains that the LoD coverage factor
  - Is based on the 95 % confidence interval
  - The 95 % interval for avoiding false positive readings is 1.65.
  - The 95 % interval for avoiding false negative readings is 1.65
  - Therefore the total coverage factor 3.3
  - This is normally rounded down to 3 for the LoD.

- The smaller coverage factor in EN 45544:2015 means there is a lower certainly that false positive or negative readings are avoided.

Instrument evaluation example

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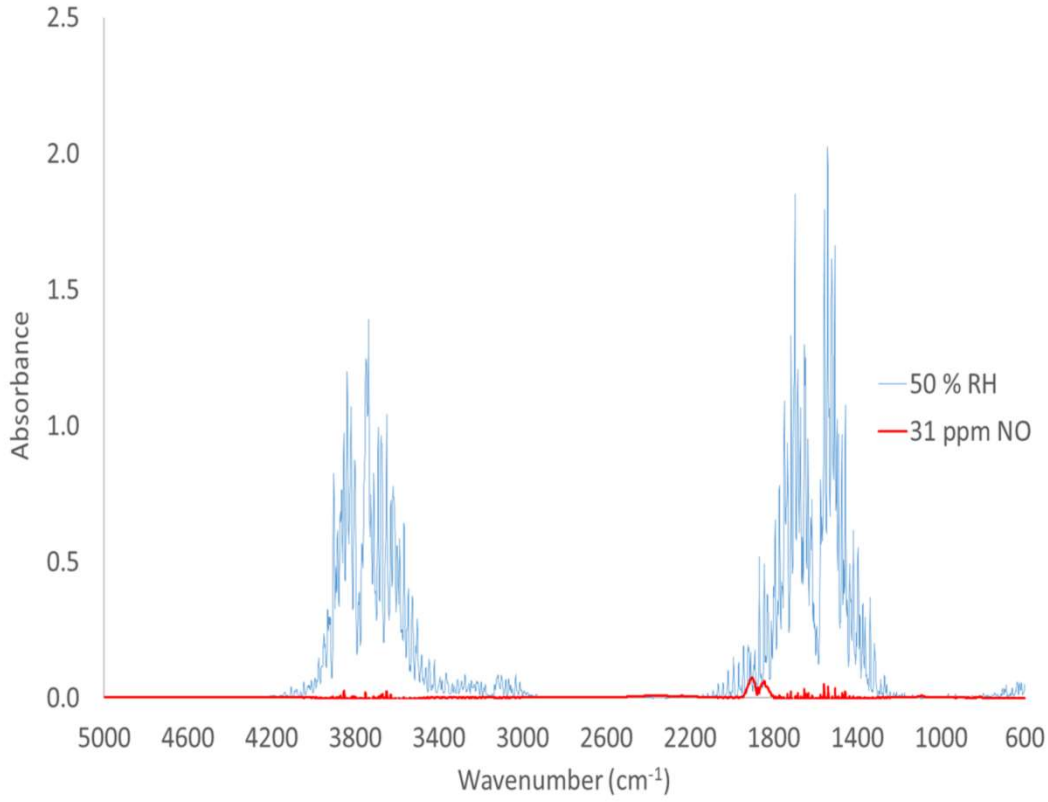
Nitric oxide determination on an FTIR

- Fourier transform infrared analyser (FTIR)
- Determining nitric oxide (NO) and nitrogen dioxide (NO_2)
- Uses a bespoke algorithm
- Evaluation was performed in a mixture of certified and in-house gas standards
- N_2 used was filtered through a scrubber assembly to remove residual NO_x
- Repeated assessments performed with increasing range of co-contaminants
  - H_2O
  - H_2O and carbon dioxide
  - H_2O, carbon dioxide and R134a



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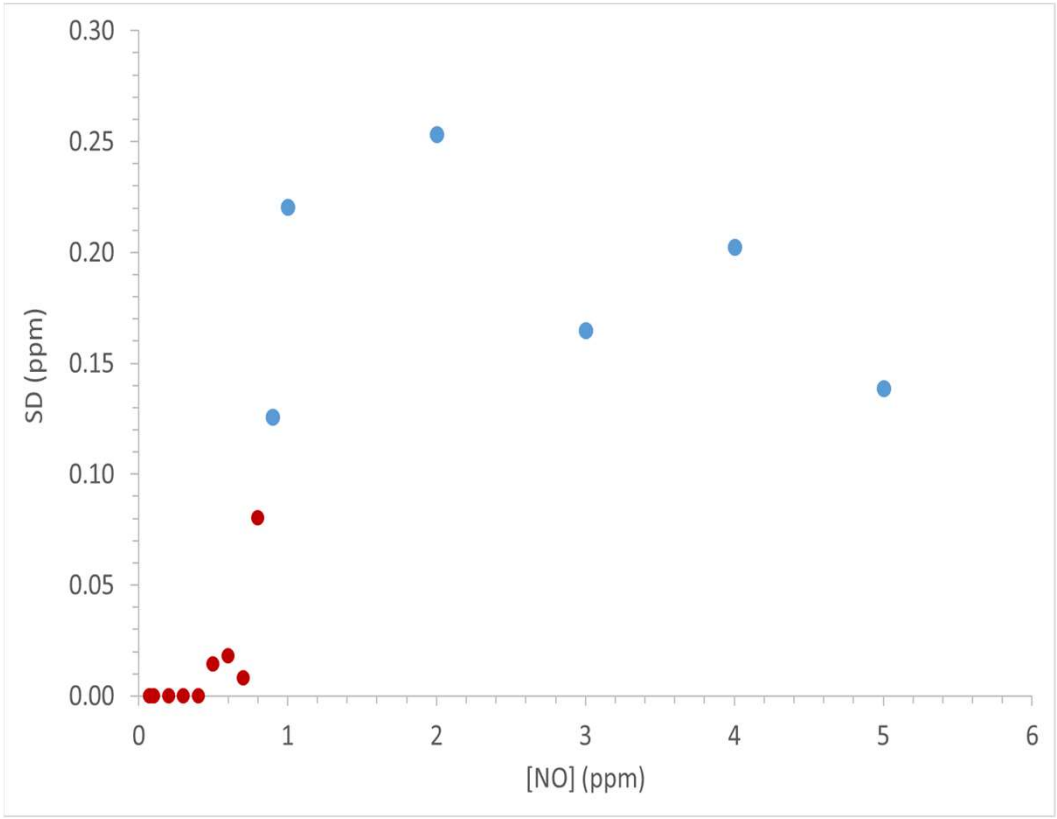
Standard deviation vs concentration

- s_0' vs concentration shows the variance due to the limited number of samples
- The FTIR does not allow the reporting of negative values
- Marked decrease in standard deviation at concentrations < 1 ppm due to false zero readings
- In reagent free gases it is not possible to assess these false zero results.



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Calculated lower operating limits

Challenge gas composition	s_0 (ppm)	U_{zero} (ppm)	LoD (ppm)	LoQ (ppm)
N_2	0.00	0.00	0.00	0.00
1 ppm NO in N_2	0.09	N/A	0.27	0.90
1 ppm NO, 50 % RH in N_2	0.22	N/A	0.66	2.20
1 ppm NO & 0.5 % CO_2 in 50 % RH N_2	0.13	N/A	0.39	1.30
2 ppm NO, 0.5 % CO_2 & 25 ppm R134a in 50 % RH N_2	0.08	N/A	0.24	0.80

- $unr_{zero} = 0.00$
  - Possibly due to processing of negative readings
- NO concentrations selected to avoided false negatives
- High variance in the humidified N_2
  - Observed in all H_2O co-contaminant tests

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Conclusions

- Understanding the method the instrument processes negative readings is important
- EN 45544:2015 does not address any matrix effects in setting the Lower Limit of Measurement
- Smaller confidence interval in EN45544:2015 give less certainty that false positive and negative readings are avoided.
- Overall this causes EN45544 to have a Lower Limit of Measurement is not achieved in real world applications.

Acknowledgements

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Submarine Delivery Agency

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Any questions

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