

Atmosphere Monitoring – Assessing functional limits of detection

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Abstract

The UK Ministry of Defence has developed its own regulations for atmosphere control in submarines (BR1326). The UK Health & Safety Executive, and the European Union, continues to drive down chemical exposure limits for Industry and these are published in The Health & Safety Executive UK EH40 guidance document. Submarine Maximum Permissible Concentration (MPC) action levels for atmosphere contaminants must be reviewed when revised evidence of the risk to health of exposure becomes available.

Understanding the Limit of Detection (LoD) and Limit of Quantification (LoQ) achievable by on-board monitoring techniques is particularly important for Royal Navy submarines because continuous MPC action levels are typically lower than Workplace Exposure Limits and consequently are more challenging for monitoring techniques to achieve. Typically the upper limits of detection and quantification are less critical in the submarine environment and these are not addressed in this paper.

A number of alternative methods of assessing the lower operation limit of analytical techniques are routinely used. For direct reading toxic gas monitors sold in Europe this is most commonly performed to EN 45544:2015 [1] whilst retrospective analysis techniques are typically based on the in-house quality requirements of the individual laboratories. Eurachem Method Validation Working Group give guidance on how to determine LoDs and LoQs in their guide, The Fitness for Purpose of Analytical Methods [2]. This paper looks at the process used in both the EN 45544 and Eurachem methodologies and how this affects the confidence in the lower operating limit. It is especially important to use a single methodology for assessing the functional limits of methods when comparing real-time monitoring techniques against retrospective methods to allow a fair unbiased assessment.

1 Introduction

Under its duty of care, the UK Ministry of Defence (MoD) must ensure that Royal Navy (RN) submarines maintain a safe breathable atmosphere. To achieve this, the MoD adopts a rigorous Passive and Active atmosphere control programme which has been discussed in previous SAMAP papers.

The submarine's atmosphere is consistently monitored and controlled within set exposure reference values (detailed in the UK restricted publication BR1326 - Book of Reference for Submarine Atmosphere Control) [3]. These levels are set to ensure that submariner health is not compromised, and so operational capability of the platform is maintained

The UK MoD has for the last twelve years, run a contract with QinetiQ to provide scientific support to atmosphere control under the Maritime Strategic Capability Agreement (MSCA). The contract objective is to assist the UK MoD in providing assured support to critical capabilities. The life support section for Submarine Atmosphere Control, consists of six specialist scientists which assist the MoD in providing scientific support / evaluation, and

targeted and underpinning research on atmosphere management techniques. This paper focuses on work on addressing the minimum operational limits of monitoring techniques performed under this contract.

2 Definitions

For the purpose of this paper the Lower Limit of Measurement (U_{zero}) is defined in accordance with EN 45544-1:2015 as ‘smallest value of the measured quantity within the measuring range’. The LoD is defined as the lowest level of an analyte that can be detected, with sufficient confidence, within the sample matrix and LoQ are defined as lowest level of an analyte that can be quantified, with sufficient confidence, within the sample matrix.

3 EN 45544:2015

Most manufacturers of direct reading gas concentration instruments selling instrumentation within Europe validate their equipment to EN 45544-1:2015. As part of this validation process the standard requires the manufacturer to calculate the U_{zero} . This is determined using Equations 1 to 4 from 10 measurements of clean air that is free of the target analyte and any other matrix contaminants.

$$ur_{zero} = \sqrt{\sum_{i=1}^n \frac{(x_i - \bar{x})^2}{n-1}}$$

Where

ur_{zero} = Random element of zero uncertainty

x_i = Zero measurement

\bar{x} = Mean of repeated zero measurements

Equation 1

$$unr_{zero} = \sqrt{\left(\frac{\bar{x}}{\sqrt{3}}\right)^2 + \left(\frac{x_{res}}{2 \times \sqrt{3}}\right)^2}$$

Where

unr_{zero} = Non – random element of zero uncertainty

x_{res} = Resolution of the indicating device

Equation 2

$$u_{zero} = \sqrt{(ur_{zero}^2 + unr_{zero}^2)}$$

Where

u_{zero} = Total zero uncertainty

Equation 3

$$U_{zero} = 2 \times u_{zero}$$

Where

U_{zero} = Lower limit of measurement

Equation 4

4 Eurachem guidance

The methods for determining the minimum concentrations of a gas contaminant that can be reliably measured by retrospective techniques are more varied. Where the laboratory is working to a national or international standard the process for determining these may be defined within the standard, although the inclusion of this requirement is not uniformly adopted by all standards committees. If the process is not defined in the standard then the test laboratory should be using a documented in-house procedures for calculating the LoD and LoQ as part of their quality system. The Eurachem Guide, The Fitness for Purpose of Analytical Methods [2], is often used as a basis of these in-house procedures and gives clear guidance on assessing a broad range method performance characteristics including techniques for determining the LoD and LoQ. The Eurachem approach requires the repeated measurement of samples that are either analyte free or with an analyte concentration close to the expected limit of determination. These samples are prepared using the normal sample matrix and therefore should contain other contaminants that are routinely present. The Eurachem method recommends the use of 10 replicate readings to calculate an estimated standard deviation s_0' using the formula given in Equations 5 to 9. Once s_0' is determined a coverage factor of 3 is applied to estimate the LoD and a coverage factor of 10 to estimate the LoQ.

$$s_0 = \sqrt{\sum_{i=1}^m \frac{(z_i - \bar{z})^2}{m - 1}}$$

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

Equation 5

$$s_0' = \frac{s_0}{\sqrt{r}} \text{ when readings are not retrospectively blank corrected during use}$$

$$\left(\text{or } s_0' = \frac{s_0}{\sqrt{\frac{1}{r} + \frac{1}{r_b}}} \text{ when readings are retrospectively blank corrected during use} \right)$$

Where

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

Equation 6

For instruments where each reading is considered to be independent and no blank correction is applied Equation 6 simplifies to:

$$s_0' = \frac{s_0}{\sqrt{1}} = s_0$$

Equation 7

$$LoD = 3 * s_0'$$

Equation 8

$$LoQ = 10 * s_0'$$

Equation 9

5 Coverage factors

The Eurachem Guide gives a clear explanation of the statistical basis for setting the LoD coverage factor which estimates the point at which there is 95 % confidence that false positive and false negative readings are avoided. These are derived from assigning the critical value where there is only a 5 % probability of obtaining false positive readings. One tailed, student t test tables give a coverage factor of 1.65. However, as false negative readings are also important an additional coverage factor of 1.65 is required giving a total factor of 3.3 which is normally rounded down to 3 for the LoD. A more rigorous statistical treatment that includes degrees of freedom gives an overall coverage factor of 3.7. There is no equivalent justification given in EN 45544 for the setting of the coverage factor used in determining the U_{zero} value, however, as this uses a smaller coverage factor on the same number of data points the confidence interval will be lower and hence there is a lower certainty that false positive or negative readings are avoided.

6 Portable oxides of nitrogen monitor

QinetiQ was recently tasked by the UK MoD, under the Maritime Strategic Capability Agreement, to perform an in depth assessment of the LoD and LoQ for oxides of nitrogen (NO_x) on a portable Fourier Transform infrared (FTIR) analyser. Some of the nitric oxide (NO) data from this study will be used in the remainder of this paper to highlight the differences in the estimated lower operational limits predicted by the two methods previously discussed and highlight why caution is required with either approach.

This study involved the exposure of the instrument to a series of both in-house and certified NO and (NO_2) gas standards over the 0 – 5 ppm range. Initially exposure standards contained the analyte in nitrogen (N_2) and then sequentially adding water vapour (H_2O), carbon dioxide (CO_2) and 1,1,1,2-tetrafluoroethane (R134a). During each exposure 10 readings were taken to allow the calculation of, U_{zero} , LoD and LoQ under each condition.

Figure 1 show a plot of the calculated s_0 results for exposures to NO standards in humidified N_2 . The software for the FTIR under evaluation does not permit the reporting of negative readings and therefore towards the lower operation limit the instrument becomes prone to reporting zero. In this figure points coloured blue are the s_0 values for datasets that only contained readings >0 . Points coloured red are s_0 values which have been artificially lowered by the inclusion of zero reading in the data set. Instruments that record both positive and negative results do not show this affect. It is therefore important, when determining the lower operation limit, to understand how the instrument reports results in this region to avoid artificially lowering the predicted detection limits.

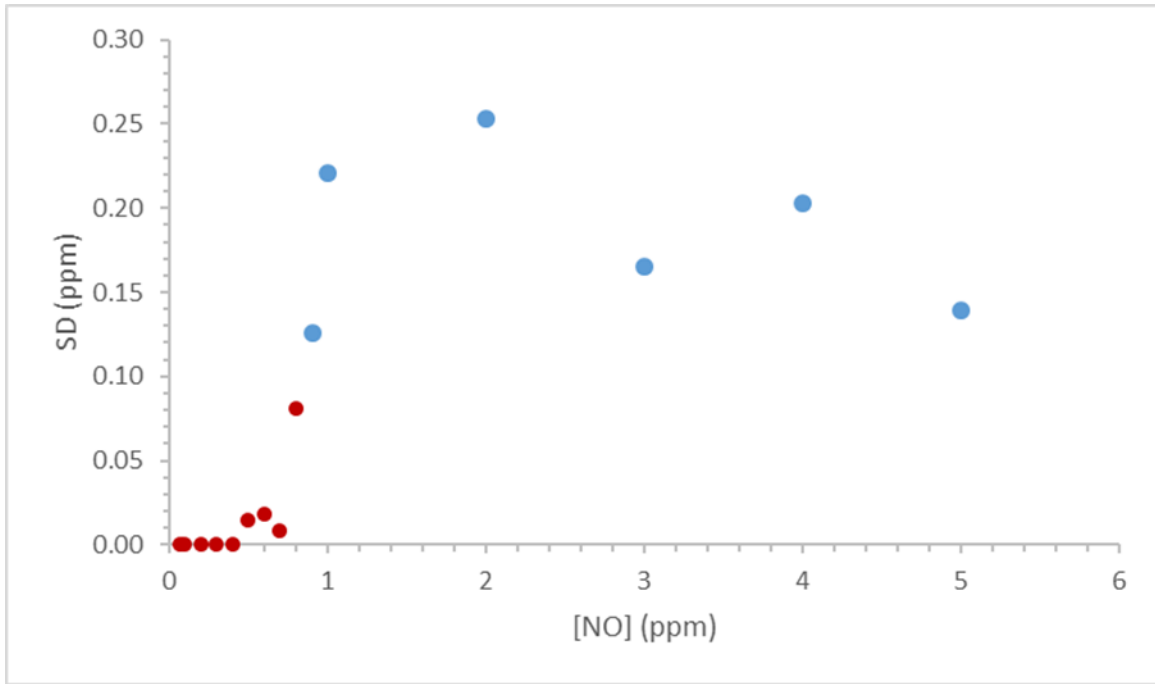


Figure 1: s_0 results for NO in N₂ at 50 % relative humidity

Table 1 shows the calculated U_{zero} , LoD and LoQ values. The s_0 value produced by exposure to contaminant free N₂ returned 0.00 ppm readings although based on results in Figure 1 it is probable that these results do not reflect the actual variance in the data that would have been observed had the software also reported negative results and therefore the U_{zero} , LoD and LoQ values are probably artificially low. Since the EN 45544:2015 method is only applicable to analyte free measurements there is no data for U_{zero} for the NO test mixtures. The results shown in Table 1 are for the minimum concentration of NO which did not report zero readings to avoid skewing the estimation of LoD and LoQ. It was unclear why the variance in the exposures with humidified N₂ were higher than when additional contaminants were present. This was consistently seen throughout all the humidified NO concentrations challenge gases and may relate to the water correction process used in the instrument processing software. Measuring NO at trace concentrations in humidified gas is always challenging using mid infrared spectroscopy as the NO absorption bands predominantly lie under the water absorption bands. The relative intensity of 50 % relative humidity N₂ and 31 ppm NO are shown in Figure 2.

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	2.40

Table 1 Calculated U_{zero} , LoD and LoQ results for NO

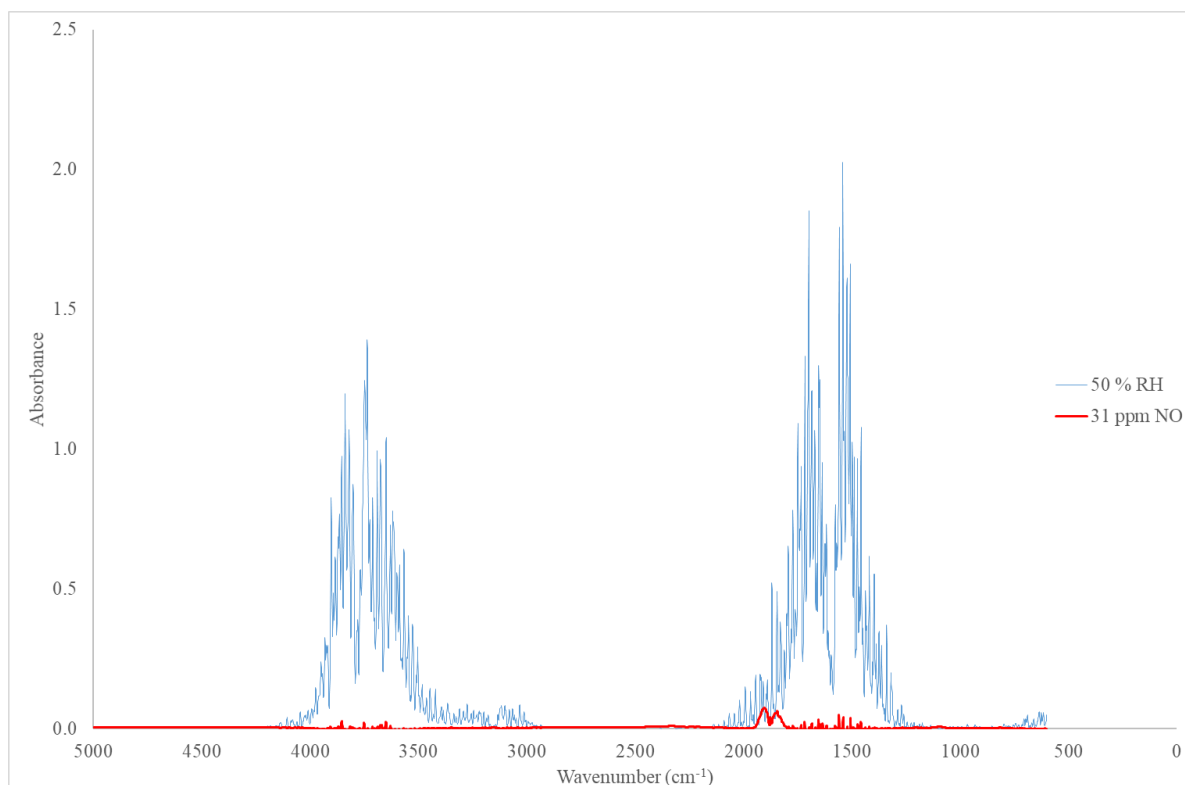


Figure 2 Mid-infrared spectra 31 ppm NO in dry air and 50 % RH N₂

7 Conclusion

Most direct reading toxic gas monitoring equipment sold in Europe state their Lower Limit of Measurements based on EN 45544:2015. This methodology uses the same number of replicates in determining this lower operating limit as the Eurachem methodology but uses a small coverage factor and therefore has a lower degree of confidence for the U_{zero} limit than a Eurachem LoD. This results in lower quoted operating limits which may not reflect the performance of the instrumentation in real world applications.

When performing assessments of the operating limits of a monitoring technique the assessor must be aware of how the instrument processes readings which would be negative values as systems that report these readings as zero artificially lower the calculated operating limits.

[1] BS EN 45544-1:2015 Workplace atmospheres – Electrical apparatus used for the direct detection and direct concentration measurement of toxic gases and vapours – Part 1 General requirements and test methods.

[2] B. Magnusson and U. Örnemark (eds.) Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics (2nd Ed. 2014).

[3] Naval Authority Group/Submarine, *Regulation for atmosphere control in submarines*, Ministry of Defence, BR1326 Ed 7, March 2016. Restricted Document.