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## Why the Limit of Detection (LOD) Value is Not an Appropriate Specification for Automotive Emissions Analyzers

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# Why the Limit of Detection (LOD) Value is Not an Appropriate Specification for Automotive Emissions Analyzers

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## ABSTRACT

With the need for emission measurements of super ultra low emission vehicles (SULEV), analyzer manufacturers have been required to produce more precise and accurate analyzers. In order to compare analyzers, the customer must understand the different specifications used by the analyzer manufacturers. One specification that some manufacturers have used is the limit of detection (LOD) to indicate the reliability of the analyzer output at low concentrations.

There are various methods for determining the LOD for a given analyzer. The authors will demonstrate how variations in methodology can produce different LOD values for a specific analyzer and what it means for the automotive emission analyzers. It is also demonstrated that the standard deviations of a zero signal, which is related to LOD, can be heavily influenced by data processing, such as data length in use and/or data smoothing. The LOD values obtained will be compared to the limit of quantification (LOQ) for that analyzer. In order to evaluate the utility of LOD measurements, various analyzer performances will be modeled and evaluated.

While the LOD is a valid statistical approach to determining the presence of a component in a sample matrix, it is not directly applicable to emissions measurements. A discussion about the emission measurement requirements will demonstrate the limited applicability of this analyzer specification. Alternative methods for comparing analyzer specifications will be presented and justified.

## INTRODUCTION

With the advent of more stringent emission regulations the analyzer limitations are becoming more critical. Previous emission levels were well above ambient levels and relatively easy to measure with established sampling and analyzer technologies. Automobiles attempting to meet ultra low emission vehicle (ULEV) and especially SULEV requirements will have to push measurement technologies to their limits. Previous papers have discussed the sampling systems for low emission vehicles, such as the CVS or bag mini-diluter [1-8]. In order to deal with very low concentrations, analyzer specification terminology has been re-introduced into the emissions field by various manufacturers.

In some cases, the LOD has been introduced for indicating performance of automotive emission analyzers. While a lower value for LOD is desirable, the specification cannot be used directly to determine what concentrations can be measured in emissions. The LOD is simply the lowest theoretical value that a signal can be differentiated from the analyzer's minimum noise level. The LOD is a measurement of the noise of a specific analyzer while zero gas is flowing. In theory and practice, the user cannot successfully quantify a concentration at the LOD.

There is a significant practical difference in automotive emission measurements from other analytical measurements where the LOD is specified. Certification measurements are comparisons between the sample bag and an ambient bag. This means that whether one could statistically differentiate a sample bag reading from the zero gas is irrelevant. The ambient bag reading is always subtracted from the sample bag reading

regardless of the measurement value. The obtained LOD should represent the performance of the whole measurement system, including both analyzers and sampling system such as the CVS. The current methods for LOD determination do not utilize the sampling system.

## LIMIT OF DETECTION

**DEFINITION OF LOD** - There are various methods for calculating the limit of detection [9-14]. Most of these methods involve the statistical analysis of the analyzer signal during blank tests, readings with the zero gas flowing. Equation 1 is the typical formula for calculating the LOD [9]. The constant,  $k$ , is the defining ratio for the LOD. The value of  $k$  is typically 2 or 3. While various authors and the International Union of Pure and Applied Chemistry (IUPAC) recommend  $k=3$  [9-11], the typical value used in industry is  $k=2$  [12]. Some manufacturers use values as low as 1.81 [13]. There are alternative LOD methods that do not use Equation 1 [14]. The LOD is similar to the expanded uncertainty,  $u_c$ , described by the National Institute of Standards and Technology (NIST) [15].

$$LOD = k \times s_{zero} \quad \text{Equation 1}$$

where,

$LOD$  is the limit of detection (LOD);

$k$  is the constant for defining LOD; and

$s_{zero}$  is the standard deviation of the zero signal or blank signal.

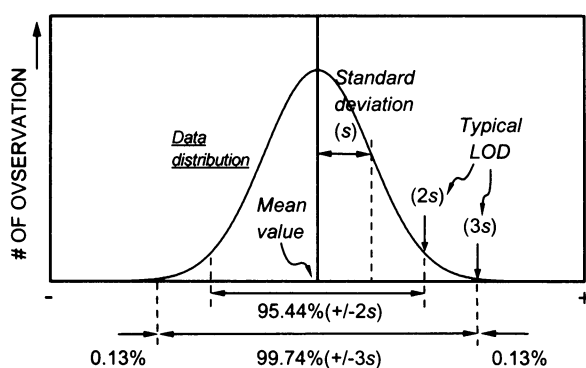


Figure 1

Figure 1 shows a Gaussian distribution curve that is assumed for measurements taken from a single sample [16]. For a blank test, the mean value would be zero. The arrows on the left indicate the relationship between the analyzer reading and the LOD. In this case, 95.44 % of the measurement readings shall be in the range between  $-2s_{zero}$  and  $2s_{zero}$ , and 99.74 % of those shall be between  $-3s_{zero}$  and  $3s_{zero}$ . If the values smaller than the

negative limits can be ignored, 2.28 % of the zero signal values is outside of  $2s_{zero}$  region, and only 0.13 % is outside of  $3s_{zero}$ . This is the reason why 2 or 3 are typically used as the constant  $k$  for the LOD (see Equation 1). Therefore, any reading greater than the mean value +  $2s_{zero}$  would be classified as the presence of the measured component at a concentration greater than zero.

**LOD AND ANALYZER RESOLUTION** - Figure 2 shows a model for distinguishing between a zero signal and a sample signal. When  $k=3$  is used to determine the LOD, the smallest sample signal that can be statistically identified from zero signal should show an average of more than twice the LOD ( $6s_{zero}$ ). In this model, the standard deviation of the sample signal values,  $s_{sample}$ , is assumed to be equal to  $s_{zero}$ . In this example, 0.13 % of the zero signal values and 0.13 % of the sample signal values will be incorrectly identified. If the average of sample signal is smaller than  $6s_{zero}$ , or the  $k$  in use is smaller than 3, the probability for an incorrect identification will increase.

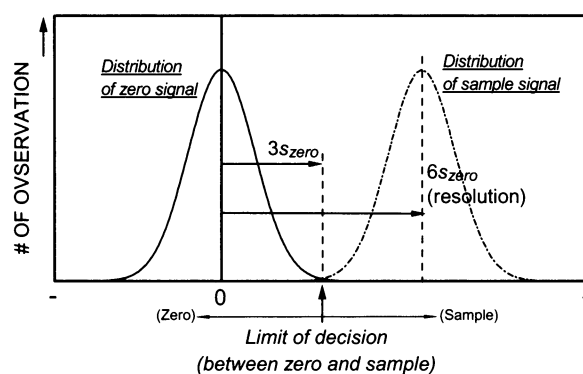
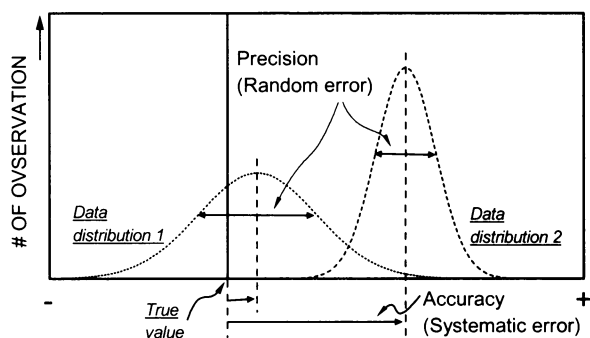


Figure 2

The typical LOD is calculated with the standard deviation of zero signal values. It only represents random error (precision) of the measured values. On the other hand, factors that are related to systematic error (accuracy) are inevitable in analyzers for automotive emission measurements. The difference between the precision and the accuracy is shown in Figure 3 as a schematic drawing. In this representation, the analyzer producing the left trace has less precision and a larger LOD. The accuracy of this analyzer is greater (closer to the true concentration) than the more precise analyzer with a smaller LOD on the right. This representation illustrates that the LOD is insufficient as an indicator of accuracy for such analyzers. Twice the value of the LOD ( $k=3$ ) can be an estimate of the "resolution" of the analyzers, because resolution means the minimum limit of distinguishable difference of two signals. The true resolution of the analyzers would require the distribution of the analyzer readings of the sample signal.



**Figure 3**

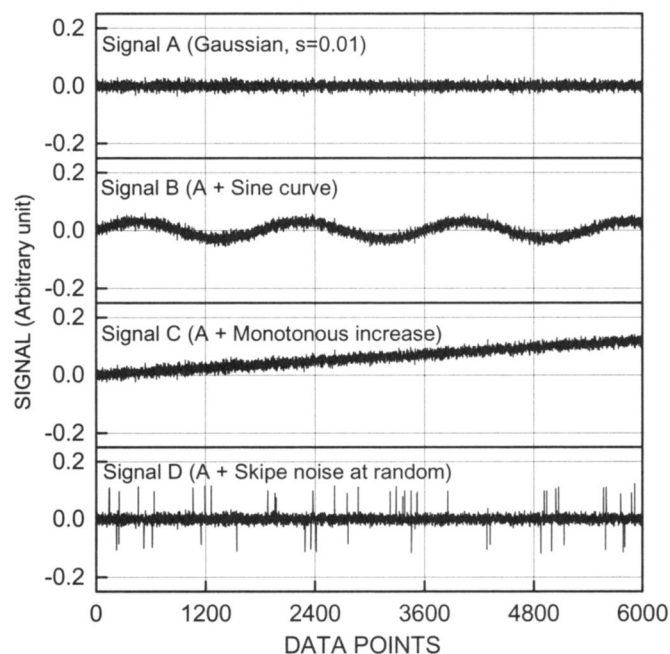
**NOISE** - The standard deviation of the zero signal,  $s_{zero}$ , is the noise of the analyzer and is dependent upon many factors. Noise can be broken down into intrinsic and extrinsic factors. Examples of intrinsic noise include dark current, shot noise and thermal (Johnson) noise. Extrinsic noise would be contributed by environmental factors such as vibration, radio frequency interference and ambient thermal changes. When used to report a detector's LOD the analyzer is allowed to stabilize over a long period of time with zero gas flowing. The portion of the signal chosen to determine noise is typically a very flat region of the trace. When measuring noise for very short periods only the intrinsic noise is measured. When measuring noise over longer periods, both the intrinsic and extrinsic noise contributions are measured.

Each analyzer converts a chemical value (concentration) to an electrical signal (voltage, capacitance or current). This signal is then amplified and measured (typically after digitizing the analog signal). This measurement in counts or voltage then utilizes a mathematical function to generate a concentration reading for a given signal. Each measurement taken with the analyzer will have an error or variation. This variation is first produced in the analyzer. As the signal is produced, amplified and digitized an error is generated at each step. The sum of all these errors in the analyzer and electronics can be viewed as the noise of the signal.

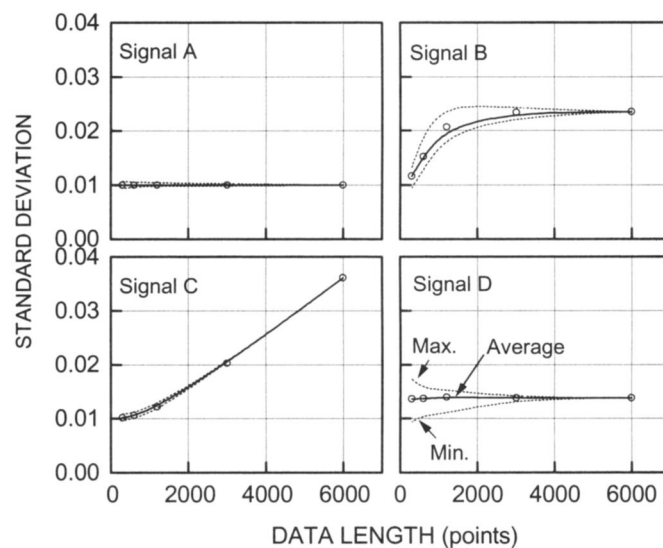
Requirements for certification in emissions testing involve the accuracy of the measurement at a point [17-21]. These measurements are all made relative to a calibration gas. A span gas is used to determine an analyzer's response to a given concentration. The user must consider this span concentration as absolutely accurate.

**NOISE SIMULATION** –Figure 4 shows simulated zero signals with four kinds of noise. Signal (A) is a theoretical simulation of random noise (6000 points) generated to match a Gaussian distribution. The signal shown with this trace is representative of the intrinsic noise of an analyzer. The standard deviation for this simulated signal is 0.01 ppm. The lower traces in Figure 4 are generated with extra noise factors superimposed onto signal (A). A periodic variation (B), a monotonic

increase (C) and a series of random (frequency and magnitude) spikes (D) were used as extra noise factors to more accurately simulate analyzer signals with extrinsic noise.



**Figure 4**



**Figure 5**

Figure 5 shows the variation of the standard deviations of the noise simulation. Calculations were done for each signal using different number of data points. For example, the data length of 300 points generated 20 standard deviations from the total 6000 points. Solid lines in the figure express average values of the

standard deviation, and broken lines show the minimum values and the maximum values among the results.

For signal (A), the standard deviation values appear to be independent of the number of data points used. On the other hand, standard deviations from signal (B), (C) and (D) vary greatly with sampling size. Long data collection times resulted in large standard deviations for signals (B) and (C). These large values are produced by the drift associated with the extrinsic noise simulation. It is presumed that data length longer than 6000 points would produce even larger standard deviations for signal (C). The standard deviations generated from signal (B) seem to be converging at about 2.4 times the intrinsic noise of trace (A). The standard deviations fluctuate greatly for short data lengths of signal (D). However, the averaged standard deviation is stable with regards to the data length. In the case of signal (D), averaging the standard deviations from many blocks of short length can be considered to be equivalent with calculating standard deviation from a block of long length. The minimum standard deviation of short sampling times approaches the standard deviation of trace (A). This is simply the standard deviation of a portion of the trace without any added spikes.

Manufacturers typically report the lowest LOD value taken over a short period of time to eliminate the extrinsic noise (drift, cyclical responses and noise spikes). Signals from analyzers always contain some level of extrinsic noise. Manufacturers are constantly trying to reduce extrinsic noise. It can be argued that reporting the minimum standard deviation with very short sampling times will characterize the actual intrinsic noise; this approach ignores the affect of the extrinsic noise on the analyzer's performance.

DATA HANDLING CONSIDERATIONS – When making an LOD determination one must consider the sample collection frequency and the amount of smoothing and filtering. The simulated signals shown in Fig.4 were subjected to 5, 10, 20 or 50 point averaging and standard deviation values were calculated from each averaged signal. The results are summarized in Figure 6. Signals (A) and (D) are in good agreement with theoretical values predicted in Equation 2.

$$s_{ave} = \frac{s_{ori}}{\sqrt{n_{ave}}}$$

Equation 2

where,  
 $s_{ave}$  is the standard deviation of averaged data;  
 $s_{ori}$  is the standard deviation of original data without averaging;  
and  $n_{ave}$  is the number of the points used in averaging.

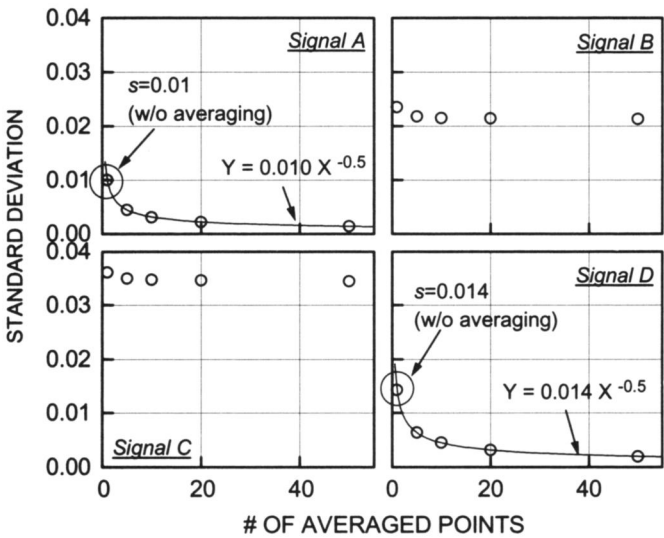


Figure 6

Averaging is less effective for signals (B) and (C). These results indicate that signal averaging is most effective for canceling the random fluctuation of noise with a shorter frequency than the averaged period. Any systematic noise that causes a drift of the average signal value will not be eliminated as effectively.

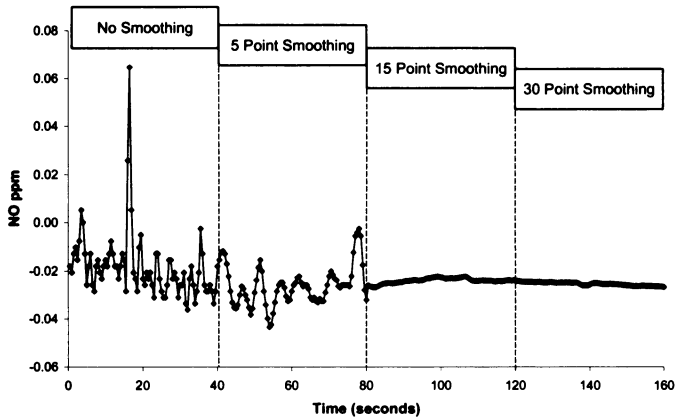


Figure 7

The data shown in Figure 7 was taken with a new Horiba CLA-720MA. The data was collected at 2 Hz. The calculated  $s_{zero}$  for the raw, un-smoothed data was 13.7 ppb measured over 40 seconds. The calculated  $s_{zero}$  for the five, fifteen and 30 point smoothed data was 8.25, 1.08 and 0.47 ppb, respectively. The almost two orders of magnitude change in calculated noise from 13.7 to 0.47 ppb with a simple smoothing function demonstrates the need to compare data handling methods when attempting to compare listed LOD values. The amount of signal smoothing used is determined by the required analyzer response times.

**UTILITY OF LOD VALUE IN AUTOMOTIVE EMISSION MEASUREMENTS**– The LOD value is used reliably for many instruments in the analytical chemistry field. The purpose of this measure was to determine a limit at which a compound could be said to be present in a sample. This is not a concept that lends itself to emission measurement methodology; the regulated compounds in emissions are always assumed to be present. The values present in the exhaust are determined after dilution (by CVS or BMD) from a bag. This bag measurement is compared to an ambient bag measurement. It does not matter if the compounds are measured at a statistically significant level above the background; the measurement values will always be used.

The LOD value is simply an indicator of a specific analyzer's noise. Manufacturers can list either the best case LOD, the LOD derived from averaged standard deviations or focus on other analyzer specifications to avoid the variability of this measurement. Under no circumstances should the user expect to reproducibly quantify signals at even three times the value of the LOD. If a customer wants to compare analyzers and uses published LOD values they must focus on the methodology used to determine these values. It should also be noted that the LOD measurement is unique to the specific analyzer that is tested and will vary between two analyzers of the same make and model. Manufacturers concentrate on reducing variability between individual analyzers but cannot guarantee uniform LOD values for every analyzer they produce.

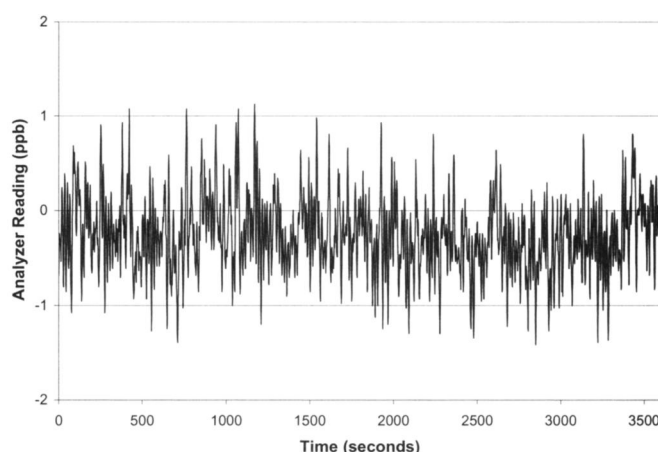
## QUANTIFICATION

**LIMIT OF QUANTIFICATION** – The LOD is not meant to indicate the lowest concentration that can be quantified. Instead, the limit of quantification (LOQ) is intended to be used as the minimum value that users of analytical instrumentation can report a value [22]. The accuracy of the number measured below the LOQ is not guaranteed. The LOQ is often reported as ten times the noise value. This would correspond to a  $k=10$  for Equation 1. If the user desires to know a reading to a given accuracy the LOQ must be determined for this accuracy. This is the lowest concentration the signal conversion curve will meet the users specified accuracy. These concepts will be applied later in this paper.

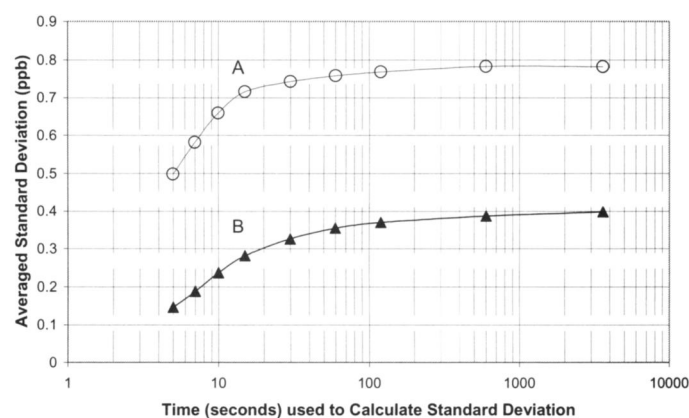
**LOD CALCULATION FROM ACTUAL DATA** - The data shown in Figure 8 was taken with a Horiba vacuum chemiluminescence detector, the CLA-750LE. The data was collected at 1 Hz with a 10 second smoothing (10 points). The averaged signal over the 6 hours was  $-0.25$  ppb.

Figure 9 shows the effect on the measurement of the noise by changing the length of time used to calculate the standard deviation. The top trace labeled A is the raw data collected at 3 Hz. The bottom trace is labeled B. This trace uses a 10 second averaged signal to determine the standard deviation. It is readily apparent

that very short times used to determine the standard deviation result in lower LOD values. The time used to calculate the standard deviation of the noise must be chosen to match the analyzer's typical measurement time. This point will be discussed later in this paper.



**Figure 8**



**Figure 9**

**SIGNAL CONVERSION** – The generation of the mathematical function converting analyzer signal (voltage, current or capacitance) to a concentration is called signal conversion. The process involves using a variety of gas concentrations to determine the analyzer signal at various concentrations. Typically a gas divider is used to mix a single span gas with a zero gas to produce numerous concentrations from zero up to the span gas concentration [23]. The CFR requires each analyzer to be calibrated using a minimum of 8 concentrations (including zero and full scale). Equation 2 is the general formula for this process where  $C$  is the generated concentration,  $S'$  is the analyzer signal (digitized or analog) and the  $A_0$  to  $A_4$  values are the signal conversion coefficients.

$$C = A_0 + A_1 S' + A_2 S'^2 + A_3 S'^3 + A_4 S'^4$$

Equation 3

**Zero and Span Calibration** – The zero calibration will determine the analyzer signal when zero gas is flowing to the analyzer. This signal will be reset to produce a zero concentration signal,  $B=S$  in Equation 4. This will correct for zero drift described in the following section. The span calibration will correct for variations in the sensitivity (span drift) for the spanned component by changing  $A$  in Equation 4. The zero calibration should be done as frequently as possible for low concentration work.  $S'$  is the adjusted signal used in Equation 3 and  $S$  is the raw analyzer signal.  $A$  and  $B$  are the calibration coefficients that are changed whenever a calibration is done.

$$S' = A(S - B) \quad \text{Equation 4}$$

This does not mean that zero level and span sensitivity just after calibration are completely accurate. Zero and span calibrations are performed using standard cylinder gases. Since the zero gases that are on the market could contain small amounts of analyzed components as impurities, a zero measurement may be offset. In addition, the accuracy of span calibration is dependent on purity of zero gas and accuracy of span gas. These are fundamental issues independent of the analyzer.

**Interference** – Composition of sample gas could possibly affect accuracy of analyzer readings as systematic error factors. For example, any differences in the oxygen content between the exhaust sample and the span or zero gas will change the zero level and the span sensitivity of FID analyzers [24]. These changes are more relevant for low concentration measurements. The amount of water and  $\text{CO}_2$  quenching on the NO measurement might cause relatively large error in low concentration measurements by CLD analyzers. Impurities in the sample bags used in the sampling system can also affect measurement accuracy [25-26]. While all these factors are very important, they exceed the scope of this paper and will be addressed in later presentations.

**Zero Drift** – One of the most critical analyzer parameters when measuring low concentrations is the signal fluctuation not generated by the analyzed component. This is most typically measured with zero gas flowing to the analyzer and is therefore referred to as zero drift. A zero calibration will correct for this analyzer drift. Analyzers intended for ULEV and SULEV measurements must reduce the zero drift as much as possible. When the zero drift is larger than the LOD or even the LOQ the zero drift masks concentration changes and produces inaccurate readings. Examples of this zero drift are represented as the simulated signal (B) and (C) in Fig. 4.

One of the parameters used to determine the LOD value that has a significant effect upon the result is the length of time the standard deviation is measured. This dependency was shown earlier in the paper. While the

instrument manufacturers want to use short measurement times to reduce the LOD values there is a practical limitation that should be applied to this time. Emission measurements from a bag are typically on the order of 15 to 45 seconds. A bag read time is typically up to 60 seconds with some of this time used to allow the analyzers to respond to the signal and stabilize. Bag reads are preceded and followed by a zero and span calibration. Any LOD measurement that is not at least 30 seconds does not take these parameters into account and is not compatible with the purpose of the analyzer. While 30 seconds might include some extrinsic noise such as drift to the LOD measurement, this extrinsic noise is part of the typical measurement and should not be removed.

**Repeatability** – Repeatability is often listed in an analyzer's specification. Repeatability is part of the precision of an instrument [27]. NIST defines repeatability as the "closeness of agreement between successive results obtained with the same method or identical test material under the same conditions." Reproducibility is defined as "closeness of agreement between the results of measurements of the same measurand carried out under changed conditions of measurement." [27]

A simplified signal conversion check procedure can be used to verify the analyzer's accuracy and reproducibility at various concentrations. The first step is to perform the zero and span calibration. This step is used to eliminate the effects of zero and span drift associated with all analyzers. After this calibration, the span gas was cut to a desired concentration. After a stabilization time, the signal is averaged to determine the analyzer's response to the gas concentration. The measured concentration is subtracted from the generated concentration to produce measurement error. The above steps are repeated at various concentrations to determine at what concentration the analyzer will no longer produce a measurement error within the customer's required accuracy. This concentration is the reported LOQ.

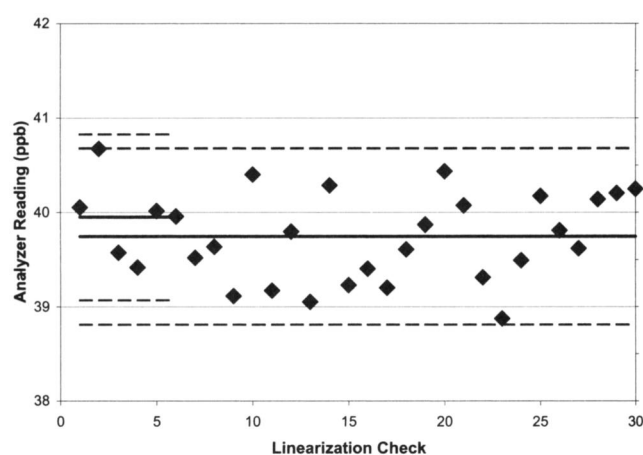


Figure 10

The number of repetitions required to generate an average repeatable value must first be determined before determining the LOQ. Figure 10 shows the results from thirty repeated signal conversion checks at a concentration of 40 ppb NO. For any repeated measurements there will always be some variation. The average of the first six data points is 39.8 ppb indicated by the first short horizontal line. The short dashed lines indicate the  $\pm 2\sigma$  error bars for this reading at (1.8 ppb). The average reading for all thirty steps is indicated by the horizontal line at 39.56 ppb. The dashed lines of the error bars for this average at  $\pm 2\sigma$  are 1.9 ppb. This data indicates that six measurements are sufficient to verify the signal conversion at a given concentration.

**ACCURACY** – The signal conversion checks were repeated six times for 8 different concentrations of NO gas. The results are shown in Figure 11. The average measurement error for each concentration is indicated by a small dash with error bars of  $\pm 2\sigma$ . By using two standard deviations, 95.5% of all measurements should fall within these error bars given a normal error curve [16]. The dashed straight lines indicate the acceptable error of  $\pm 2\%$  of the measured point. It can be seen that the measurements below 40 ppb start to have error bars that exceed the CFR required accuracy of  $\pm 2\%$  of point. Therefore, 40 ppb is determined to be the LOQ for this analyzer ( $k=54$ ). This point is labeled D. The LOQ at  $k=10$  for this analyzer<sup>1</sup> was determined to be 7.4 ppb NO and is indicated by the label C. The error bars are well outside of the  $\pm 2\%$  of point limits. The dotted lines containing the error bars at point C indicate the reduced accuracy of  $\pm 10\%$  of point. Therefore, measurements taken at or greater than the LOQ would result in an accuracy of at least  $\pm 10\%$  for this analyzer. The LOD<sup>2</sup> is indicated by label B.

Each gas concentration produced with a gas divider has an extra error in its value, the error associated with the flow controller. The two concentrations that do not have gas divider error added to the signal variability are the span gas concentration and the zero gas. This does not mean that the zero gas actually has zero concentration of the component analyzed, just that the analyzer will treat the signal generated by this gas as a zero concentration. The accuracy of the span and zero gas concentration value is dependent upon the accuracy of the cylinder concentrations and the reliability of the gas transfer system to the analyzer.

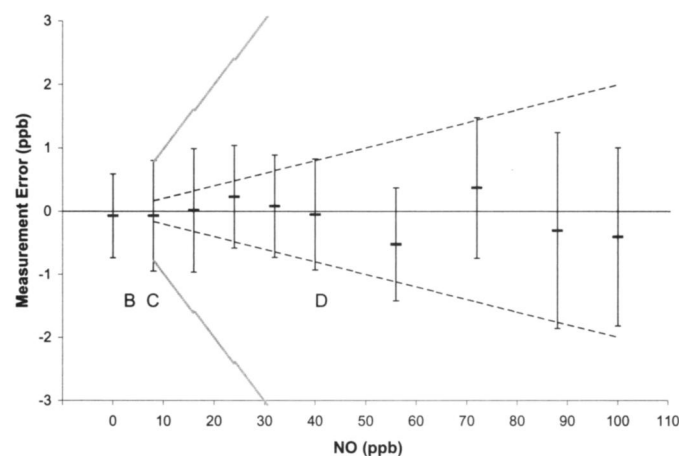


Figure 11

## CONCLUSION

The ability to measure ULEV and SULEV emission concentrations requires significant effort by the user. With the need to measure smaller concentrations, analyzer manufacturers have introduced terminology to the emissions measurement field that are new to many experienced users. The LOD and LOQ values can be useful specifications for analyzers. The problem with their usage comes from a lack of understanding about how they are calculated and how they can be used. The LOD does not indicate the lowest concentration that the user can measure. Zero drift, repeatability and reproducibility are factors that can be more significant than LOD values.

Analyzer manufacturers can obtain drastically different LOD values depending upon their method of calculation. The length of time used to calculate the noise signal will have the biggest effect on the LOD value. In order to be relevant to the emission measurement industry, the length of time used to calculate the noise should be standardized across the industry to allow more meaningful comparisons between analyzers. This length of time should be equivalent (or close to) the time used for a typical measurement with the analyzer. This time would not include the delay for the analyzer to stabilize the signal. The authors suggest 30 seconds as a significantly long period of time for data collection. Data collection times of significantly shorter duration are typical in the industry.

The user must concentrate ultimately on what is the lowest concentration that can be measured with better than 2% accuracy. Therefore, the authors feel that LOQ is a much more valuable measurement than LOD. However, determination of the LOQ should not be performed by picking an arbitrary  $k$  value for Equation 1. The use of  $k=10$  resulted in an accuracy around  $\pm 10\%$ . The LOQ should be determined to achieve an accuracy of at least  $\pm 2\%$ .

<sup>1</sup>  $k=10$ , 4 second averaging and the standard deviation determined over 30 seconds

<sup>2</sup>  $k=3$ , 4 second averaging and the standard deviation determined over 30 seconds



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## DEFINITIONS, ACRONYMS, ABBREVIATIONS

**LOD:** Limit of Detection

**LOQ:** Limit of Quantification

**NO:** Chemical formula for nitrogen oxide