Primer on DPD Chlorine Method Detection Limits and their Use in Compliance Reporting

The **Method Detection Limit (MDL)** is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, and is determined from analysis of a sample in a given matrix containing the analyte. The MDL is a qualitative value that represents a confidence that the detection is not a false positive. It is not a quantitative value but offers a 99% confidence that the detected value is greater than 0 mg/L and less than the minimum level of quantification at a 95% confidence. The MDL was originally developed to establish the lowest sensitivity of a test method in a reference matrix such as reagent water. The MDL is developed from the replicate analysis of reagent water fortified with the analyte of interest at an initial level which is 3-5 times the signal to noise of the instrument used to make the measurement. For chlorine measurement using a colorimeter, the fortified value is approximately 0.2 mg/L. Typically, seven replicates of this fortified solution are measured. The standard deviation is calculated and multiplied the student-t value for 6 degrees of freedom at a 99% confidence. The basic assumption behind the MDL determination, that precision is indicative of detectability, does not always hold true. Moreover, the procedure does not take into account the effects of high or low bias on the MDL. It is entirely possible that a series of measurements may yield a high precision (small standard deviation) but be biased either high or low. Bias may affect the calculated detection limit. Unfortunately, it is practically impossible to pinpoint a "true" detection limit for most analytes without introducing some uncertainty about the validity of low level results. If there are known interferences in the subsequent samples that will be measured by the chlorine method, a MDL may be established from a specific sample matrix. This is performed in a similar manner as above except that seven replicates of a sample matrix taken prior to chlorination are analyzed without chlorine fortification.

The **Method Limit (ML),** also known as the lowest achievable quantifiable limit at a 95% confidence is derived from the MDL. The MDL is multiplied by a factor of 3.18 to yield the ML. The ML is often rounded to the nearest 10th of a mg/L.

An example of the determination of MDL and ML is provided below. The data used in this example is actual data used by USEPA to approve the Hach Free and Total Chlorine Methods.

Spike Level for MDL Determination
0.20 mg/L

Seven replicates of reagent water fortified with free chlorine to 0.20 mg/L

Replicate #1 – 0.23
Replicate #2 – 0.23
Replicate #3 – 0.23
Replicate #4 – 0.22
Replicate #5 – 0.22
Replicate #6 – 0.21
Replicate #7 – 0.22

Standard deviation = 0.00756

MDL = 3.143 * 0.00756
MDL = 0.024, rounded = 0.02 mg/L Cl

ML = MDL * 3.18
ML = 0.02 * 3.18
ML = 0.06 mg/L Cl
Rounded ML – 0.1 mg/L Cl

Minimum Disinfectant Residual

The minimum disinfectant residual level is a compliance level set by some States and USEPA. Typically, this value is set to 0.2 mg/L Cl. This level is approximately 4 times the minimum quantitation limit (MDL) and 2 times the lowest quantitation limit (ML) that was determined above.

Minimum Detectable Disinfectant Residual

The minimum detectable disinfectant residual level is a compliance level set by some states. Typically, this value is set to 0.02 mg/L. This value is the MDL for chlorine as determined above. It is a detectable only value (uncertainty of quantitation) that has a concentration range that varies from 0.02 mg/L to 0.05 mg/L.

Interferences with DPD Chlorine Chemistry

All DPD chemistry products for the measurement of free chlorine are subject to interferences by iron and manganese. When these analytes are present in the matrix the measured DPD value is total free oxidants that respond to DPD. DPD values as result from iron and manganese cannot be subtracted from the sample value to obtain free chlorine.

ALL DPD chemistry products for the measurement of total chlorine are subject to interferences by iron and manganese.   When these analytes are present in the matrix the measured DPD value is the sum of total oxidants that respond to DPD. DPD values as result from iron and manganese cannot be subtracted from the sample value to obtain total chlorine (free chlorine plus chloramines).