Understanding the Limit of Detection
Lovibond® PTV Series of Process Turbidimeters

By Michael J. Sadar
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Introduction:

The limit of detection (LOD) is a specification that is often used in process (on-line) analytical methods. Its use in process turbidity measurement is of particular interest when filtration systems are being optimized. This is because the drinking water treatment optimization process will yield filter effluent turbidities that are far below any regulatory levels. For example, many water plants will establish filter effluent limits that are below 0.1 NTU, which is significantly lower than the USEPA 0.3 NTU regulatory limit for drinking water filtration. As water plants strive to produce better and more consistent water, they need to understand the limits of their monitoring systems. In the case of filter effluent monitoring, turbidity is the key parameter that is used.

Simply explained, the limit of detection for turbidity is the smallest true change in turbidity that can be detected by an instrument. It is one specification of many that is commonly used to determine the quantitation limits for a given instrument. This level must be above the sum of the electrical, optical, mechanical and fluidic noise floors of the analytical system. When applying the LOD to on-line instrumentation, it should be derived under normal operational conditions of the instrument. These conditions include a calibrated system, operating within the range of typical sample flow, and the manufacturer’s prescribed use of any measurement algorithms (these are typically recommended in the user manuals). These conditions have an impact on the LOD of an on-line analytical system.

The practical use of the LOD is to provide the defined detection level for a given analyte. In filter effluent turbidity measurement, slight changes in turbidity that are above the detection limit are indeed real and this information can be used to optimize the performance of the filter and potentially the treatment process upstream.

An important practical use for the LOD is in the setting of a 4-20 mA range. When setting this range it is important to understand the smallest step change within the range be approximately equal to or above the limit of detection. If the smallest step change (4-20 mA resolution) is below the LOD, then a single step change in the analog to digital signal may not be due to turbidity.

For example, if the instrument LOD is 0.0005 NTU, and the analog to digital converter (in a PLC that accepts the instrument 4-20 mA signal) is 12-bit, and the desired 4-20 mA range is 0-1 NTU, would the smallest step change in the 4-20 mA signal be real? For a 12 bit conversion, then this range of 0-1 NTU would be divided into 212 or 4096 steps. Thus, the value of each step is 1/4096 = 0.00024 NTU. If this value is approximately equal to or slightly above the instruments LOD, then this would be a suitable range for the 4-20 mA setting. In this example, a single step change would be below the LOD and may not represent a change in turbidity. Actually, it would take two steps, which would be a change of 0.00048 NTU, to approximately equal the 0.0005 NTU LOD. Or, it would be better to simply double the overall 4-20 mA range to 0-2 NTU, of which 2/4098 = 0.000048 NTU, which is then approximately equal to the LOD of 0.005 NTU in this example.
LOD Test Methodology

The LOD is derived from a special test in which the test instrument's sample stream is spiked with an analyte (in this case a defined turbidity value) that is at a level of about 5 percent of the appropriate measurement range of interest. Once the response to the analyte spike is achieved, the standard deviation of the measurement system (in this case is the instrument with sample flowing through it) is determined. The derived standard deviation is then multiplied by 3 to generate the LOD value or by 10 to generate the limit of quantitation (LOQ).

A referenced test method for LOD determination is found in the International Organization for Standardization (ISO) 158392. This test instructs to spike an analyte to a concentration that is approximately 5 percent of the working range of the instrument. The variance of the measurement of that spike is ultimately used to derive the LOD. Since turbidimeter designs can have an overall range that often covers several orders of magnitude, the test can be modified to a spike level at 5 percent of the lowest applicable range. Since the applicable operating range is typically below 1 NTU for drinking water applications, then the spike should be approximately 0.05 NTU above the sample turbidity baseline.

To perform a spike on a process instrument, the sample stream should be of a stable low turbidity. In the case of LOD determination, the sample stream should be filtered to remove any residual turbidity. This is often referred to as the blank. This can be accomplished through pushing the water through a 0.1 µm or smaller nominal pore size filter. The filtrate (effluent) stream will generally have a very low turbidity that is theoretically about 0.010 NTU. Note that the theoretical limit of turbidity is a function of many factors including wavelength and respective bandwidth of the incident light, stray light, and detector sensitivity. When the standard deviation of the 0.05 NTU spike is determined, it is multiplied by a factor of 3, to yield the LOD value. The standard deviation is derived from a group of 30 consecutive measurements of the turbidity spike, once the instrument has delivered full step response of the spike. This is repeated until seven sets of spike data have been determined and then the average of these spikes is the published LOD.

Figure 1 shows the test set-up for LOD determination. The figure shows three test instruments, a PTV 1000 with a white light LED, a PTV 1000 with an 860-nm (IR) LED and a PTV 2000 with a 660-nm LED. The sample is the filtered water source. It flows at a constant and known flow rate. The injection standard which delivers the turbidity spike is formazin is of a defined turbidity value. It is pumped at a known and constant rate into the sample stream. The spiked sample then travels through a mixing coil to ensure homogeneity of the spiked sample prior to it being split into the three test instruments. Spent sample and excess sample travel to drain.

The LOD was determined using the normal or manufacturer recommended operational conditions for the turbidimeter. In the case of the PTV Series of turbidimeters, this included the use of the bubble removal algorithm and signal averaging. Most important, the test should be run with sample flowing through the test instruments.

Some LOD tests involve a dry test, without sample. This test typically will measure the instrument variance on a fixed dry standard such as a glass rod or cube. Such a test does not account for sample flow and ambient conditions that the process instruments are normally exposed.

Note: if the LOD value is not described, consult the respective manufacturer regarding the procedure that was used to deliver this specification.

Data and Results

The LOD was calculated from the standard deviation of each of the seven spikes. These were then averaged to generate the LOD for each of the test instruments. This test was also performed over different signal averaging settings for the instrument. The PTV Series signal averaging algorithm will average a consecutive number of measurements that take place at a frequency of once per second. Thus, 30 second signal averaging involves the averaging of the last 30 readings, and a 90 second signal involves the averaging of the last 90 measurements.

Table 1 provides a summary of the calculated LOD and then the LOQ for the three different models of the PTV Series of Turbidimeters. The table illustrates the impact that signal averaging will have on the limit of detection. Signal averaging will impact LOD determinations, with longer signal averaging leading to slightly lower (better) LOD values. Figure 2 provides a graphical presentation of the LOD data between the three versions of the Lovibond® turbidimeters. In all cases, the LOD values are below 0.001 NTU with no signal averaging and below 0.0005 NTU when 30 second or greater signal averaging is used.
The tradeoff with the use of higher signal averaging is that the response time to a turbidity event will increase. However, if the level of quantification (LOQ) is derived from the LOD (which is 3.34 times the LOD value) the LOQ for the PTV Series of turbidimeters is still less than 0.001 NTU when the signal averaging is set to 30 seconds or longer. This value is below all reporting requirements for existing regulatory turbidity methods around the world. The 30-second signal averaging is the default setting for the PTV Series of instruments.

Conclusions:

The Limit of Detection is an important specification for low-level process turbidity monitoring. The LOD will provide information on the lowest turbidity that can be detected by the instrument which is important when setting the ranges and step changes for analog outputs. The LOD is also related to the LOQ, which is the lowest reliable quantifiable reading that can be delivered. When used according the manufacturer’s recommendations, the PTV Series of turbidimeters deliver LOD and LOQ values that exceed the established criteria in existing regulatory requirements and demonstrate the detection and quantification sensitivity that is required for low-level turbidity measurement.

The Lovibond® PTV Series of turbidimeters were approved by the USEPA for the measurement of Drinking Water turbidities. Combined with their LOD and LOQ they are suitable for use in the monitoring of filter effluent turbidities and the optimization of drinking water processes.

### Table 1 – Calculated LOD and LOQ for PTV Turbidimeters Using Different Measurement Algorithms

<table>
<thead>
<tr>
<th>Test</th>
<th>Average LOD Value (7 Spikes)</th>
<th>Averaged LOD (LOD*3.34)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PTV 1000 WL NTU</td>
<td>PTV 1000 IR FNU</td>
</tr>
<tr>
<td>Bubble Reject (BR) Only</td>
<td>0.000584</td>
<td>0.000872</td>
</tr>
<tr>
<td>BR and 30 second Sig Avg</td>
<td>0.000103</td>
<td>0.000062</td>
</tr>
<tr>
<td>BR and 60 second Sig Avg</td>
<td>0.000065</td>
<td>0.000035</td>
</tr>
<tr>
<td>BR and 90 second Sig Avg</td>
<td>0.000056</td>
<td>0.000042</td>
</tr>
</tbody>
</table>

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**Figure 1** - Test setup to produce a defined low turbidity spike that is necessary for limit of detection determination.
Figure 2 - Graphical representation of the LOD for the Lovibond Series of Turbidimeters. Data is presented on a log scale.

References: