Technical Note
YSI, a Xylem brand • XA00140

EXO NitraLED™

CORRECTIONS FOR TURBIDITY AND NOM

INTRODUCTION

The YSI **EXO NitraLED**™ sensor detects Nitrate using the basic principle of optical absorbance. All optical technologies must contend with Turbidity interference, which occurs due to the scattering of light caused by suspended particles. Sensors that rely on the UV ranges of light will experience NOM (Natural Organic Material) interference due to absorbance. This technical brief describes how the NitraLED sensor works, focusing on the NOM and Turbidity corrections as they are applied to the raw signals within the sensor.

BASIC CONSTRUCTION OF THE EXO NitraLED SENSOR

The sensor has a primary LED that emits light of 235 nm to interrogate a water sample. Multiple species of nitrogen will absorb 235 nm light, and the NitraLED sensor cannot distinguish between these different species. Nitrite, for example, will also absorb. However, in natural waters, Nitrate is typically the most prevalent species.

Within the sensor, NOM is detected with a LED that emits light of 275 nm. Like other NOx species absorbing at 235 nm, NOM is not the only thing in natural waters that can absorb 275 nm light. But within certain ranges, and especially with user-provided inputs about the environment, the 275 nm LED can facilitate NOM corrections to in situ measurements. The efficacy of the correction depends upon the nature of the NOM.

Turbidity is handled by leveraging the EXO Turbidity sensor. This sensor must always be used alongside the NitraLED sensor. Veteran EXO users already know that the Turbidity sensor works on the principle of light scattering, which is different from absorbance. How the EXO Turbidity sensor assists in the correction for Turbidity attenuation is described below.

Nitrate is measured in units of Nitrate as Nitrogen. Thus where chemical formulas are used, NO_3-N will be written. This is because the sensor is factory-calibrated in a NO_3-N standard and the calibration standards for

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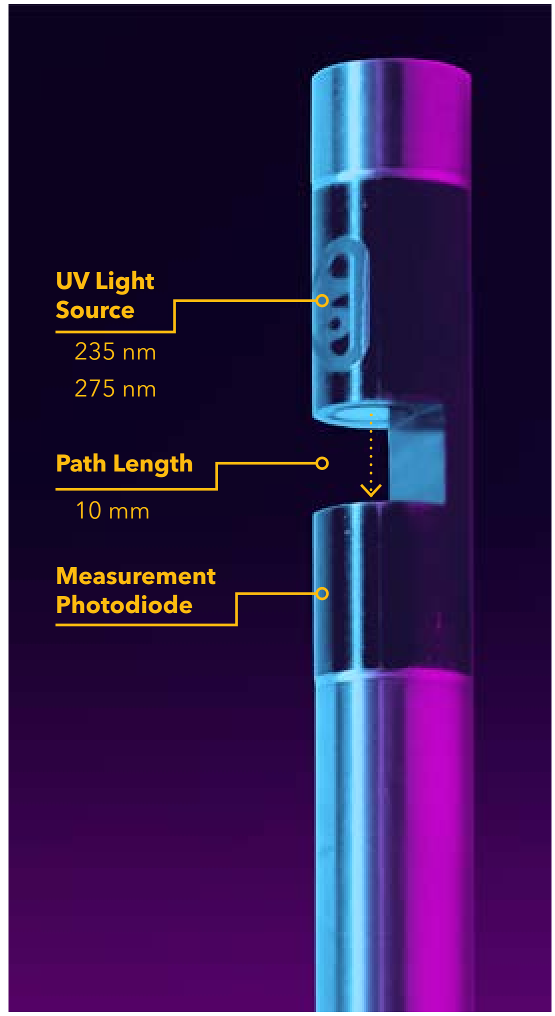
user calibration are also NO_3-N when purchased from YSI. Due to the attenuation effects that have been so carefully addressed within the sensor, any particulates or irregularities in standards that can impact the quality of calibration, and thereby the accuracy of measurement, the YSI standards are the only ones where this effect is known not to happen. Other standards will work with NitraLED, but these risks should be noted.



PRINCIPLES OF ABSORBANCE

The EXO NitraLED sensor uses optical absorbance to calculate Nitrate concentrations. Absorbance is measured in absorbance units, AU, and follows Beer's Law:

$$A = -\log\left(\frac{I_t}{I_o}\right)$$

where A is absorbance in AU, I_t is the intensity of light transmitted through the sample, and I_o is the intensity of light as it originates from the sensor.

A very simplified equation for how the NitraLED sensor computes absorbance of Nitrate based on the total absorbance at 235 nm recorded by the sensor is:

$$A_{235} = A_{NO3\text{-}N} + A_{Turb235} + A_{NOM235}$$

The effects of interferences are determined using a similarly simplified equation at the 275 nm wavelength:

$$A_{275} = A_{Turb275} + A_{NOM275}$$

The absorbance at 235 nm is determined using Beer's Law and then the attenuation due to Turbidity, which will have been converted to AU, and absorbance from NOM, estimated from 275 nm, are subtracted. The $A_{NO3\text{-}N}$ thus calculated will be used in a regression equation that is based upon the factory linearization and then two-point user calibration.

This regression defines the relationship between absorbance and Nitrate concentration. It is imperative in the calculation of this regression that the Nitrate standards used during calibration have no absorbance from any particulate matter or organic compounds. As stated earlier, this is among the reasons that it is recommended to purchase the standards from YSI.

HOW CORRECTIONS ARE MADE IN KOR SOFTWARE

Kor Software allows EXO NitraLED users to calibrate and perform corrections to optimize the sensor for their specific measurement site. This process involves three key steps:

1. Enter a Nitrate value for a site-collected sample, determined by an independent measurement
2. Correct for Turbidity by either:
   a. Using the default turbidity coefficients made available in the software, or
   b. Estimating Turbidity attenuation by making measurements of both raw (unfiltered) and filtered water from the site
3. Correct for NOM using a slider bar to optimize output based on the filtered site sample

First, the EXO NitraLED and Turbidity sensors must be calibrated before proceeding with the site-specific corrections. A grab sample must be collected from the measurement site for the correction process. The sample's Nitrate concentration, in mg/L, should be determined by an independent method, such as an EXO ion selective electrode (ISE) or a benchtop photometer.

For Turbidity, the easiest approach is to use the software's default Turbidity coefficients. There may be advantages to a site-specific correction, however, and this will have to be decided by the user. In that case, the NitraLED sensor will be used to compare measurements of a sample as it is collected, and again after it is filtered using a 0.45 μm filter.

As a final step, NOM corrections are made using a slider bar to optimize the sensor output in filtered water. This is detailed in the last section of this technical brief.

CORRECTING FOR TURBIDITY ATTENUATION

Turbidity can have a significant effect on absorbance measurements, as it can scatter the light on its path from the LED to the detector. The number, size, and shape of particles can all influence the level of light attenuation. As seen in Figure 1 below, the relationship between the "absorbance" of 235 nm light and Turbidity FNU is fairly linear. However, the slope of that relationship varies with different sources of Turbidity. The default absorbance correction programmed inside the NitraLED sensor is based on Kaolin (example in figure). This was chosen because it very nearly approximates the average of all the samples YSI worked with. Some of the samples (Miami River and Canoe Club) in Figure 1 were in fact collected from natural waters, while the others (Bentonite, Arizona Test Dust, Diatomaceous Earth, Kaolin, and Elliot Silt Loam) were purchased. It was verified that the samples were nitrate-free in the case of the purchased

standards, and field samples were corrected for Nitrate when it was present. The graph shows only the 235 nm wavelength correlations, but a similar linearity was observed for Kaolin at 275 nm.

When a user chooses the default Turbidity coefficients in Kor software, the relationship between Kaolin and absorbance is applied to the raw signals within the sensor. An average set of Kaolin interference correction coefficients are used based on extensive testing; all of the Kaolin tests conducted are not depicted in Figure 1.

A user may instead choose to do a site-specific correction. For example, Figure 1 demonstrates that at higher FNU, the difference between samples grows. If users work with higher FNU waters, they may not find these differences acceptable for their study objectives.

For example, the Turbidity at a site could be 120 FNU and the absorbance measured by an optical tool (spectrophotometer, NitraLED, etc.) is found to be 0.19 AU. The slope of the equation with site-specific Turbidity is 0.00158 AU/FNU. By comparison, the slope of Kaolin is 0.0028 AU/FNU. Therefore we see that depending on the sediment type, the difference between the default absorbance correction and a site-specific correction can have a significant effect on the NitraLED's calculation of Nitrate. When one uses the site-specific correction, NitraLED builds a new Turbidity regression equation internally, which will override the use of the default relationship for processing the raw signals in the sensor. During the site-specific correction process, an absorbance value is collected before and after the sample is filtered using a 0.45 µm filter. This difference in AU is expected to be due to particles that were removed by the filter (*i.e.* Turbidity). This method is described in the EXO User's Manual (Rev K and later).

Note that while these measurements of Turbidity were made, NitraLED was also collecting measurements using the 275 nm LED. Conveniently then, the corresponding absorbance at each wavelength is determined and subtracted from the total absorbance measured by each sensor. We are now able to narrow down absorbance from NOM and Nitrate. The equations from the previous section then become:

$$A_{235} - A_{Turb235} = A_{NO3\text{-}N} + A_{NOM235}$$

$$A_{275} - A_{Turb275} = A_{NOM275}$$

The absorbance of NOM is now known at the 275nm wavelength but that number is not equal to the absorbance of NOM at 235 nm, which is determined as described below.

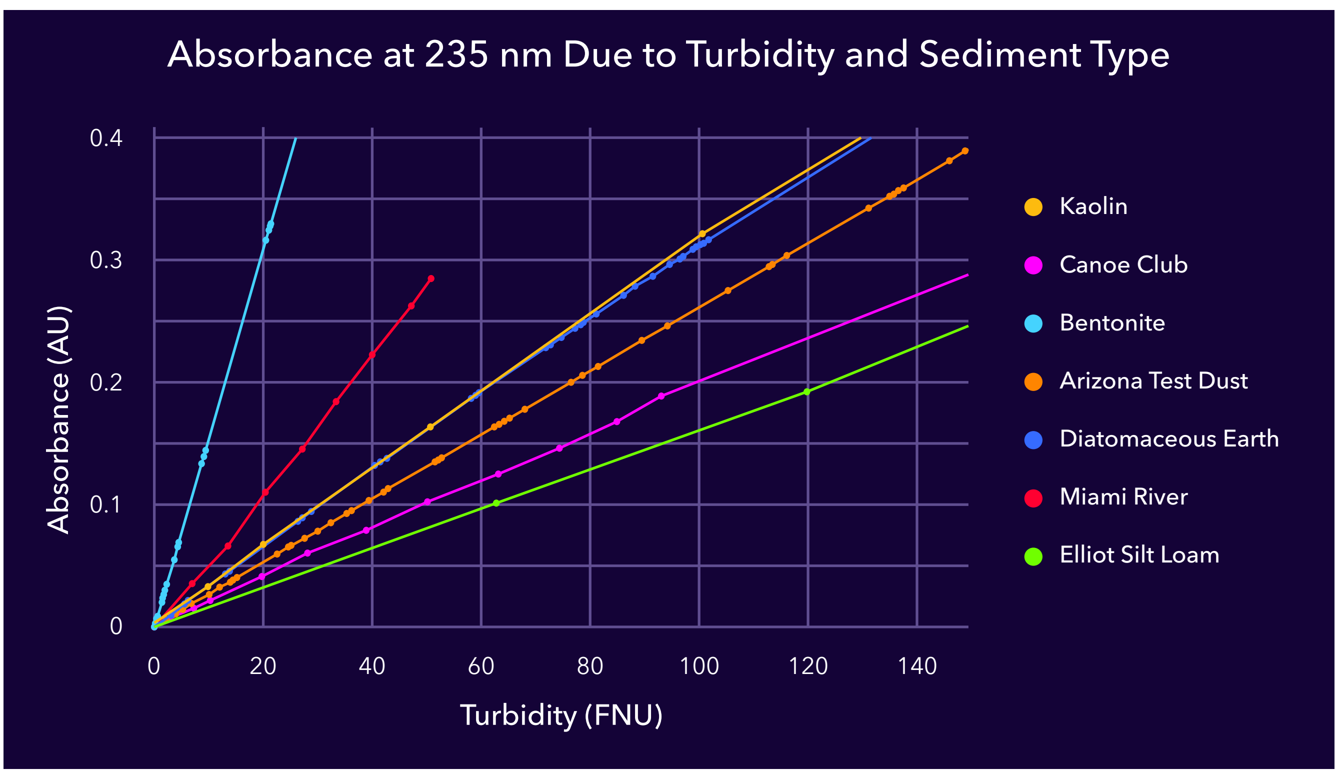


Figure 1: *The absorbance measured by the NitraLED sensor will vary depending on the sediment type and the amount of that sediment in the water sample.*

CORRECTING FOR NOM

The correction of NOM from the 275nm wavelength to an absorbance of NOM at the 235nm wavelength is loosely adapted from a Standard Method for measuring Nitrate in wastewater.[1] The NOM correction factor is equal to the following:

$$\text{NOM factor} = A_{235} / A_{275}$$

The NitraLED sensor has a default NOM coefficient programmed internally but for the most accurate calculation, it is recommended to perform a site-specific correction. In the site-specific correction procedure, a slider bar is used to make minor adjustments to the above ratio. As this number is adjusted, the output of the sensor is adjusted, and tweaks to the NOM coefficients should be made until the output is equal to the known Nitrate concentration. Recall that this Nitrate concentration will have been made with an independent measurement.

Once the NOM factor is determined, the absorbance of NOM at the 235nm wavelength is determined following rearrangement of the equation above:

$$A_{NOM235} = \text{NOM factor} * A_{275}$$

This calculated NOM at 235 nm is used in the equation below to determined absorbance measured by NitraLED that is attributable to Nitrate:

$$A_{NO3\text{-}N} = A_{235} - A_{Turb235} - A_{NOM235}$$

Once the absorbance of Nitrate has been calculated, it is then inserted into the regression equation stored in the sensor during the two-point calibration process to determine the final estimated concentration of Nitrate in the measured sample.

The above description of the sensor calculations describes how a Nitrate value is computed but the procedure for the site-specific correction was not adequately defined. For complete instructions on how to perform the site-specific correction procedure, please reference the EXO User Manual.

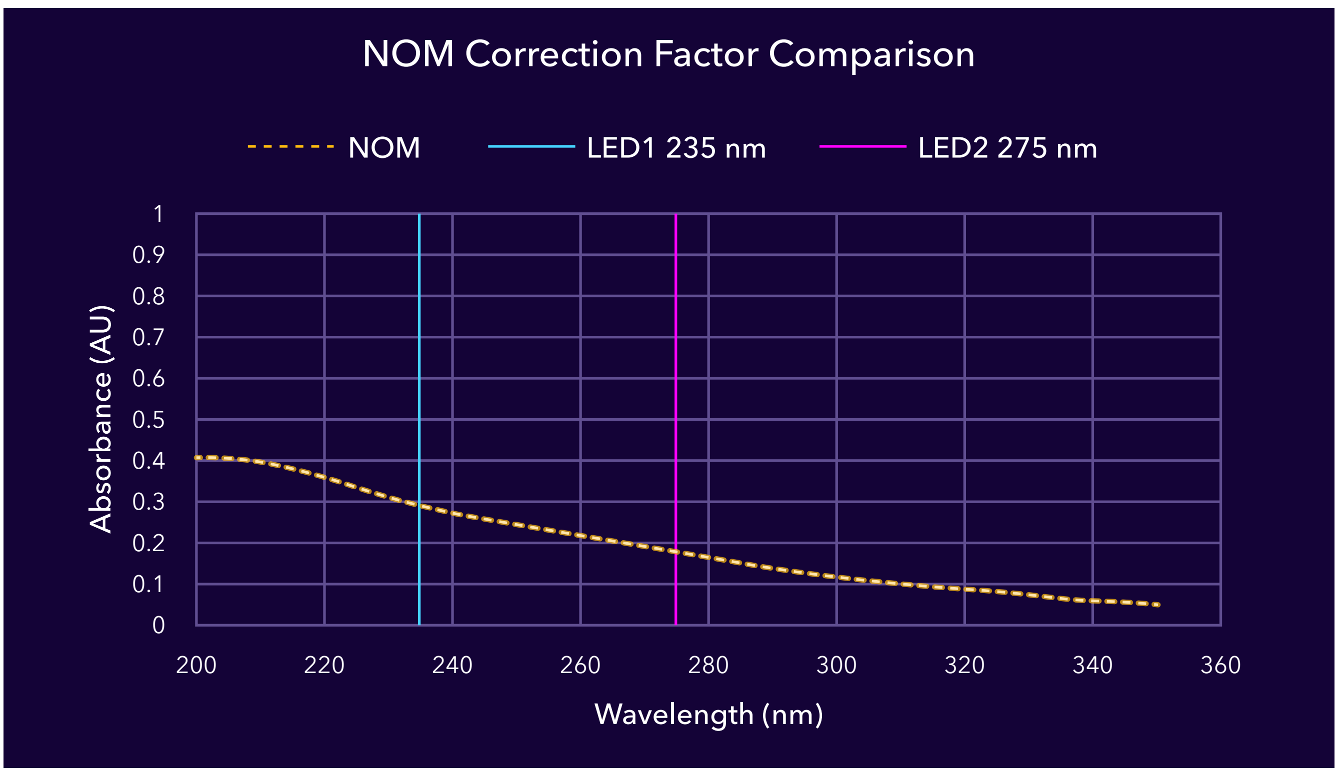


Figure 2: *The NOM correction factor is equal to the absorbance of NOM at 235 nm divided by the absorbance of NOM at 275 nm. The absorbance of NOM measured by each wavelength can vary by site*

[1] "4500-NO3-NITROGEN (NITRATE) (2017)", Standard Methods for the Examination of Water and Wastewater. DOI: 10.2105/SMWW.2882.089

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