Turbidity – Clarifying Low Level Measurements

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In the past 10 years, the analysis of turbidity has become far more than just a measure of water clarity. Now, low level turbidity analysis is becoming the method of choice for protection against emerging pathogens such as Cryptosporidium and Giardia. By assuring proper water filtration, risks from a variety of undesirable contaminants in our nation's water supplies can be reduced.

In 2002, the EPA published the LT1ESWTR (Long Term 1 Enhanced Surface Water Treatment Rule) mandating turbidities in combined filter effluent to read at or below 0.3 NTU. The EPA hoped this action would achieve a 2 log (99%) removal of Cryptosporidium1. There is presently consideration to lower this to 0.1 NTU. To achieve the EPA's goals, constant turbidity monitoring of filtered water is critical. This monitoring is often accomplished with the use of on-line turbidity meters at water treatment plants and with portable instruments in the field. The trend has been to check the calibration of on-line turbidimeters with either bench-top or hand-held field turbidimeters using precision standards created to meet EPA specifications.

Turbidity Measurement

Before venturing too deep into the subject of water clarity, it makes sense to discuss the basic principles of turbidity measurement. Turbidity is an aggregate property of water. It is caused by suspended particles in water. It is not specific to the type of particle in the water and the particles can be suspended or colloidal matter, as well as inorganic, organic or biological. At high concentrations, turbidity is perceived as cloudiness, haze, or an absence of clarity in the water.

Turbidity analysis is an optical measurement of scattered light. When light is passed through a water sample, particles in the light path change the direction of the light, scattering it. If the turbidity is low, most of the light will continue in the original direction. Light scattered by the particles allows the particles to be detected in the water, just as sunlight can illuminate dust particles in the air.

A turbidimeter is a general term for a meter that measures turbidity. Measuring low level turbidity requires precisely quantifying the scattering of light in water using a turbidimeter that is also a nephelometer. The terms nephelometer and turbidimeter are often used interchangeably, as they are here. However, a nephelometer specifically measures light scattered at a 90° angle to the light beam. Light scattered at other angles may also be measured, but the 90° angle defines a nephelometric measurement. The light source for nephelometric measurements can be one of two types to meet EPA or ISO specifications. The EPA method specifies a tungsten lamp, with a color temperature of 2,200 – 3,000 K2. The units of measurement for the EPA method are recorded as nephelometric turbidity units (NTU). The ISO method specifies a light emitting diode (LED), with a wavelength of 860 nm and a spectral bandwidth less than or equal to 60 nm3. The units of measurement for the ISO method are formazin nephelometric units (FNU).

The use of portable hand-held nephelometers to check the calibrations of on-line turbidimeters/nephelometers requires the hand-held meters to have meticulously designed optical systems. These meters must be capable of stable, long-term calibrations, high precision and accuracy, and low detection limits. Even with a well designed meter, measurement technique is critical to obtaining accurate and precise low-level turbidity readings4. Measurement techniques include selection and use of sample tubes, minimizing stray light interference, and proper sample handling.

Tube Selection

The selection and handling of the tubes is of utmost importance. Tubes may occasionally need to be soaked in a dilute HCl solution before washing. They should always be washed on the inside and outside with mild detergent prior to use, to remove dirt or fingerprints. The tubes should be rinsed 5 – 10 times with turbidity-free water. They should then be allowed to air-dry in an inverted position to prevent dust from entering the tubes. Clean, dry tubes should be stored with their caps on to prevent contamination. Prior to use, tubes must be clean and free from lint, fingerprints, dried spills and scratches. Scratches are especially a problem if they are located where the light beam enters or exits the tube. Any tube that has been scratched should be discarded and replaced with a new one.

After a tube has been filled and capped, it should be held only by the cap to avoid problems from fingerprints. When setting a filled tube aside make sure it is placed on a clean and dry surface that will not contaminate the tube. Before being placed in the instrument, the outside surface of the tube should be wiped with a clean, lint-free absorbent cloth, until it is dry and smudge-free. This is imperative for precise readings and will keep the light chamber in optimal condition. Tubes should be emptied and cleaned as soon as possible after reading a sample to prevent deposition of particulates on the inside of the tubes and caps. For highly accurate results, errors from contamination can be reduced by designating tubes and caps for use only on very low turbidity samples, while others can be reserved solely for very high turbidity testing.

Some manufacturers suggest lightly coating the outside of tubes with silicone oil. The purpose is to fill in tiny scratches and minimize stray light associated with imperfections in the tube. However, applying consistent amounts of silicone oil is a challenge and small variations can

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cause large changes in the refractive index of the tubes. This can result in substantial changes in turbidity readings. For this reason many manufacturers warn against the use of silicone oil. There are other more reliable methods for minimizing stray light.

Stray light reduction

Stray light is light that is detected but is not directly scattered from the turbidity in the water sample. Interference from stray light will cause high readings. Stray light can come from electronic noise, internal reflections within the optics, and from stray reflections from dirt and dust in the meter chamber5. Scratches, fingerprints and water droplets on the tube can also cause stray light interference, leading to inaccurate results. Contemporary turbidity meters, equipped with microprocessors, eliminate electronic noise by subtracting out a sample reading with the light source turned off. Turbidimeters that have a blanking procedure can eliminate stray light associated with internal reflections. The blank should have the same interference, due to internal reflections, as the sample and is subtracted from the sample reading to remove this source of stray light interference. If the same tube is used for the blank as for the sample, and is properly indexed in the chamber, stray light interferences due to tube imperfections can be minimized.

Another source of stray light is molecular scattering of light by the water molecules themselves. Dissolved molecules, including extremely small sub-micron particles that can not be filtered out, will also scatter light. This molecular scattering of light has been estimated to be between 0.01 NTU and 0.02 NTU. For this reason ultra-pure water can still cause light scatter and is therefore often called low turbidity water.

It can be argued that using a blanking procedure can eliminate the effects of stray light from molecular scattering. If water that has been properly filtered through a 0.1 micron filter can be considered turbidity free, because there are no undissolved particles in the water, then any stray light must be from molecular scattering. This stray light can be compensated for with a proper blanking procedure, on an instrument with high quality focusing optics, and a result of 0.00 NTU can be obtained.

Negative Results

A useful feature, for evaluating low level turbidity, is a turbidimeter that displays negative results. Meters will occasionally make a reading that is negative and should be displayed as a negative number. This situation is more likely to happen when measuring low level turbidity. Natural variations in all measurements, instrument and non-instrument related, can lead to a negative result. Thus, some turbidimeters are designed to round up a negative number to 0.00 NTU, since a result of less than 0.00 NTU is theoretically impossible. However, in practice, these results are actually quite meaningful. If a meter consistently gives a negative result, there is a problem. The problem could be operator technique or error. It could also indicate a problem with the low turbidity/turbidity-free water used for a blank or a problem with the calibration. If the meter rounds the negative result to 0.00 NTU, the user will not be alerted to a potential problem.

Sample Handling

Variability in the geometry of the glassware and the technique used to orient tubes in the light chamber are predominate causes for inconsistent results. Slight variations in wall thickness and the diameter of the tubes may lead to slight variations in the test results. To eliminate this error the tubes should be placed in the chamber with the same orientation each time. Many turbidity tubes have indexing lines for this purpose. Even better than an indexing line are orientation devices that physically force a tube to be positioned in the same orientation every time. For improved accuracy and precision, especially at low concentrations, some form of orientation device is highly recommended.

Before adding the water sample to a tube for a turbidity measurement, the tube should be carefully rinsed 3 to 5 times with the solution, whether it is a blank or a test sample. The tube should then be capped immediately to prevent dust or other contaminants from entering the tube. Be sure not to spill water on the outside of the tube. If there is a spill, immediately wipe the tube clean before dry deposits can form.

For low level turbidity, the tube should be allowed to sit for several minutes to degas after adding the sample. Tiny invisible bubbles of dissolved gasses can cause a positive interference in the results. Degassing with a vacuum can lead to contamination if extreme care is not taken. A sonic bath can be used to degas a sample, if the tube was rigorously cleaned beforehand. If the tube was not scrupulously clean, a sonic bath can dislodge particles from the tube walls and increase turbidity6. After the sample has been degassed, the tube should be inverted gently to suspend any particles that may have settled out. The tube should then be allowed to sit and come to a quiescent state before taking a reading on the turbidimeter.

Low level readings should always be verified that they are stable by taking two or three readings on a sample or a blank. Unstable readings can result from convection currents in the sample due to mixing. A few large particles passing through the detection area of the tube can also cause unstable readings. To compensate for this some turbidity meters have a signal averaging option that allows the meter to average multiple readings on an unstable sample. Being able to observe the reading during this averaging process will let the user see if the sample is providing a stable measurement.

Studies have indicated that low level turbidity analyses are frequently affected by user techniques7. Since there is a learning curve to making good turbidity measurements, meticulous care and practice in measurement

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techniques are required for high accuracy and precision when testing low level turbidity.

Calibration

Nephelometers usually have a factory calibration for the full range when they are purchased. Regulatory authorities often require that the calibrations in these meters be verified and adjusted. Turbidity standards are required for calibration/verification of meters. Most meters are supplied with turbidity standards, such as AMCO8, SDVB (styrene divinyl benzene), formazin or "stabilized formazin," as primary standards. Primary standards are approved by the EPA for calibration of turbidimeters. Other types of secondary standards are also available but can only be used to verify a calibration.

Analysts should only use standards recommended by the manufacturer of the nephelometer. Formazin is a universal standard but dilutions are highly unstable. AMCO standards are more stable and easy to use, but must be uniquely formulated to individual meter designs. An AMCO standard designed for one turbidimeter cannot be reliably used with a different type of meter, even if these meters are from the same manufacturer. "Stabilized formazin" is stable but requires special mixing instructions that must be carefully followed. The refractive index of low level "stabilized formazin" standards is very different from low level formazin standards and from most ultra-pure low level turbidity water. However, the refractive index of low level formazin standards and most ultra-pure low level turbidity water is very similar. Differences in refractive indices can lead to very different results. A meter calibrated with "stabilized formazin" cannot be verified with formazin standards, at low levels. At high turbidity levels the refractive index differences become small and both stabilized and un-stabilized formazin should give the same results.

There is a linear relationship between the scattered light at 90° and the turbidity of water below 40 NTU. There are two different approaches to calibrating turbidimeters for low level testing. One approach uses intermediate level turbidity standards to establish the linear relationship between 40 NTU and ultra-pure water. The meter is calibrated at the intermediate level and then extrapolated backwards to measure samples below 1 NTU. One problem with this method is that any errors made in establishing the intermediate calibration point are magnified when measuring a sample farther and farther away from that point. At very low levels of turbidity, these errors could become a significant part of the measurement. The second approach to calibration is to establish linearity in the turbidity range of the samples to be measured. This is a common approach to calibrating scientific instruments. If the samples to be measured are below 1 NTU, the linearity is established by calibrating with a 1 NTU standard. Stable 1 NTU standards are available for turbidimeters that are calibrated by both approaches. The same careful measurement techniques, for making good low level turbidity readings discussed previously, are required for low level calibration. Once these techniques are learned, they become part of the process of making quality readings of all types, whether the readings are sample readings, calibration readings, or verification readings.

Turbidimeters that use a blank have a distinct advantage in establishing a linear calibration with two points in the range of samples to be tested. For low level turbidity, a turbidimeter can be calibrated with ultra-pure water and a 1 NTU standard. The use of good technique, ultra-pure low turbidity water and a stable 1 NTU standard are critical for this calibration. The result is a very well established calibration for the range of 0 – 1 NTU. Blanking the meter before reading samples always ensures that the reading of ultra-pure low turbidity water is referenced every time a sample is determined. This helps maintain a good low level calibration. It has been shown that turbidimeters that use some sort of blanking procedure, or a procedure to set a predetermined low reading such as 0.02 NTU, read lower than meters that do not use this procedure9. The difference increases over time most likely because the base line response drifts upward on meters that are not repeatedly calibrated with an ultra-pure low turbidity standard.

Summary

Reliable low level turbidity measurements are a critical water quality measurement for regulatory compliance and monitoring filtration efficacy. To obtain dependable results, careful attention to measurement technique is critical. Maintaining tubes with good optical qualities, minimizing stray light and careful sample handling are all important factors. A well designed instrument is only effective if it is accurately calibrated. Finally, referencing an ultra-pure low level turbidity standard, such as a blank, while testing samples will help preserve and verify a good low level calibration testing program.

References

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