

UV254 and True Colour Online Instrumentation

Ensuring Optimised Coagulant Dosing with Accurate UV254 and Colour Measurement

UV254 and colour measurement in water treatment works

Many water treatment works use online instrumentation measuring UV254 or colour to quantify organics in the raw water for the purposes of coagulation control. All these instruments have some method for removing the effect of turbidity on the UV254 or true colour measurement. Without this, the UV254 and colour readings would always reflect the absorbance from the organics in the raw water and light lost due to diffraction by particles seen as turbidity. These two effects – absorption and diffraction – can't be separated by measuring a single wavelength only, a turbidity compensation measurement is always necessary.

To ensure an accurate measurement of the organics only in the raw water, a robust turbidity compensation mechanism must be used, otherwise it can lead to overdosing of coagulant.

Conventional approach to turbidity compensation

Most online instruments for raw water coagulation control measure the absorbance of the water at two wavelengths. Firstly, the wavelength of interest (254nm for UV254 and typically 400nm for colour) and secondly, a reference measurement at a different wavelength to measure the turbidity. Often this reference wavelength measurement is in the visible region of the electromagnetic spectrum (e.g. 550nm). The software in the instrument then corrects the measurement absorbance for turbidity in the sample, measured at the reference wavelength. The more turbidity in the water, the larger that correction will be.

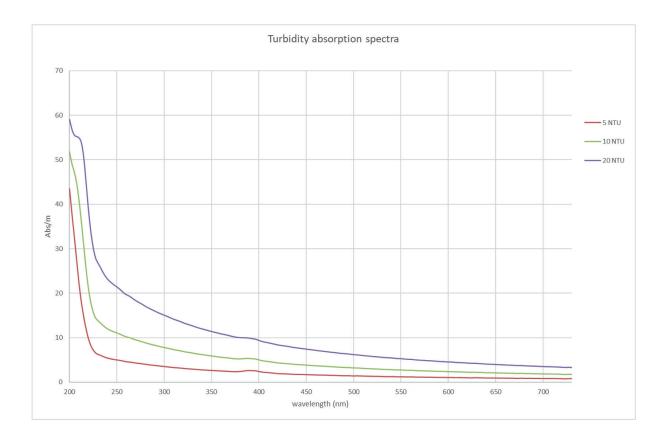
However, there is an issue with this approach. Turbidity does not affect all wavelengths equally. It is well understood when referring to turbidity measurement, that the measurement wavelength is important and different wavelengths will give different results for turbidity. For example, using a longer wavelength (such as the near infra-red wavelength used in the ISO7027 turbidity standard method) has the potential to miss smaller particles.

When it comes to absorbance, the same principle applies, the shorter the wavelength used for measurement, the more the turbidity affects the absorbance. When discussing online measurement of UV254 and colour, an instrument manufacturer must decide how they will apply their reference turbidity compensation measurement to the measurement wavelength itself.



Do they assume that whatever the absorbance is at the reference measurement wavelength should just be subtracted from the measurement wavelength absorbance? Or do they try and apply a factor to account for the fact that the absorbance at a lower measurement wavelength may be different to that at the reference measurement due to the turbidity?

The graph below demonstrates the effect of different levels of turbidity on different wavelengths. The absorption spectrum of several different turbidity standards is shown below. There are no other absorbing species in the sample.



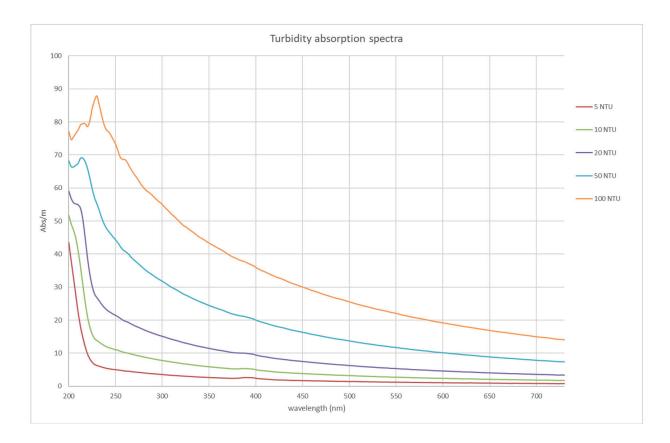
The absorbance measurement at 254 nm is 4.8 Abs/m, 10.9 Abs/m and 20.5 Abs/m between the three different standards (5, 10 and 20 NTU respectively). A reference measurement at 550 nm would measure 1.2 Abs/m, 2.7 Abs/m and 5.3 Abs/m.

NTU Standard	Measurement at 254 nm	Measurement at 550 nm
5 NTU	4.8 Abs/m	1.2 Abs/m
10 NTU	10.9 Abs/m	2.7 Abs/m
20 NTU	20.5 Abs/m	5.3 Abs/m

It is clear from this data that a simple subtraction approach to turbidity compensation, as recommended by DIN 38404-3² is not sufficient. Manufacturers must do something more complex in determining the effect of turbidity at the measurement wavelength. Using the above spectra, it could be argued that by simply multiplying the reference measurement by 4, you can establish the correct factor to apply to the measurement wavelength.



However, at higher levels of turbidity, this relationship breaks down. At 100 NTU, the absorbance at the measurement wavelength (254 nm) is 69 Abs/m, but at the reference measurement (550 nm) it is 22 Abs/m, the compensation factor has decreased, using our x4 correction factor now is not accurate. In real raw water samples, the variety of scattering of different size and shape particles complicates the relationship further.



This is why single wavelength turbidity correction models do not work very well in more turbid samples. The more turbidity, the more important it becomes to ensure the turbidity compensation approach is correct to ensure accurate measurement of the organics.

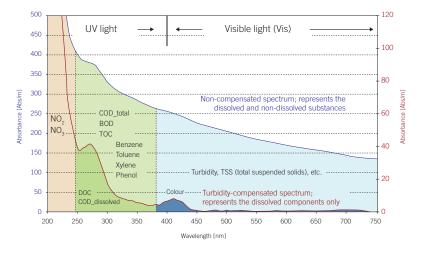
Alternative approach to turbidity compensation

The alternative approach to using a single wavelength turbidity compensation mechanism is to use the entire UV-Vis spectrum absorbance and apply an algorithm to this spectrum to account for the contribution to it from turbidity. This allows the generation of a turbidity compensated spectrum from which multiple turbidity compensated parameters can be defined simultaneously.

This method uses a mathematical equation which describes the relationship between scattering caused by turbidity and wavelength as a function of the particle diameter. The effect was first described by Gustav Mie in 1908 and is known as Mie Scattering nowadays. Practical implications of this effect for the measurement of turbidity were published by Huber and Frost (1998)¹ and includes the well-known spectral shape caused by suspended solids, which depends upon both the wavelength as well as on the particle diameter itself.



Different applications tend to have different particle types/size distribution, so it is necessary to have different algorithms for different applications. By using this approach, more accurate readings can be obtained for parameters such as UV254 (post sample filtration) and true colour.



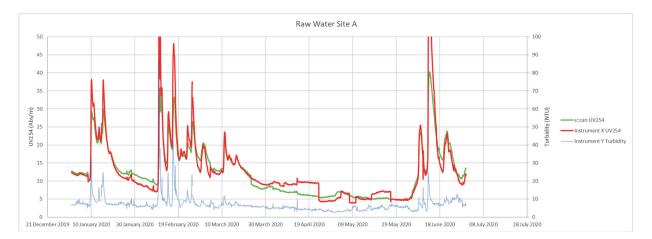
s::can Sensors

s::can are leaders in the manufacture of online UV-Vis spectrophotometers. s::can were formed in 1999 as a spin out from the "University of Natural Resources and Life Sciences, Vienna" where the original work on using the multiple wavelength turbidity compensation approach was developed. The first sensor developed was the s::can spectro::lyser which was initially designed for remote monitoring in surface water applications.

The s::can <u>spectro::lyser</u> sensor is a fully submersible online UV-Vis spectrophotometer sensor now used across the globe in a wide range of different applications and can measure anything in water that can be determined by UV or Visible spectroscopy, including nitrate, organics (DOC and TOC), colour and more. The s::can spectro::lyser sensor platform utilises the multiple wavelength turbidity compensation mechanism rather than a single wavelength turbidity compensation approach. This mechanism applies to all s::can sensors that utilise the spectro::lyser platform including the <u>nitro::lyser</u> and <u>carbo::lyser</u>.

Case Study

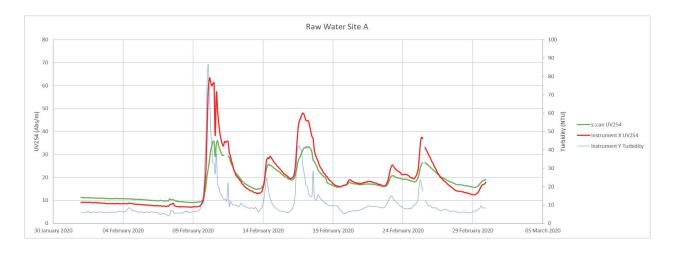
The following data is from a water treatment works where a s::can spectro::lyser monitors the raw water for multiple parameters. On the same sample, is an online UV254 instrument which uses the single wavelength turbidity compensation mechanism.





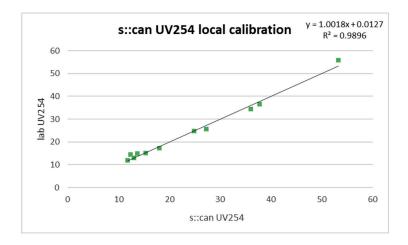
This data shows when turbidity is low (<10 NTU) correlation between the two UV254 measurements overlay one another, the only exceptions being in April when instrument X appears to drift away from the s::can reading before being brought back into line via a calibration in late April, and again in mid May.

When turbidity increases to greater than 10 NTU, we can see instrument X generally reads higher than the s::can UV254 reading. This is because of the turbidity compensation mechanism used in Instrument X. It is easier to see the effect if we zoom in to the February data.



For every peak in turbidity, instrument X reads UV254 higher than the s::can sensor and the larger the turbidity peak, the bigger the difference between the two measurements. When there is low turbidity, the two instruments correlate.

The accuracy of the s::can turbidity compensation approach when measuring UV254 was verified by comparing the results against the laboratory method. The lab sample was filtered through a 0.45 micron filter to remove turbidity before being measured with a UV spectrophotometer at 254 nm. The correlation R2 value between the two methods over several samples taken over a period of time was 0.9896.



The s::can solids compensation technique has also proven on raw water monitoring to produce accurate true colour readings even when the levels of turbidity reach above 100 NTU.



Conclusion

When deciding on a UV254 or colour instrument for coagulation control, it is important to consider the accuracy of the reading during a turbidity event. Overestimation of UV254 can lead to overdosing of coagulant. Underdosing can lead to an increased risk of disinfection by-product formation potential. During large turbidity events, this may be deemed as doing little harm to combat the increased coagulant demand associated with the increased turbidity. However, the consistent overestimation of UV254 even during relatively small turbidity increases can only lead to additional chemical dosing costs.

When choosing a UV254 or colour monitor, it is often worth understanding the turbidity compensation used by the instrument and verifying it is accurate when you most need it.

References

- 1. Huber & Frost, Light scattering by small particles, Blackwell Science, Vol 47, issue 2, 1998 https://doi.org/10.1046/j.1365-2087.1998.00086.x
- 2. DIN 38404-3 German standard methods for the examination of water, waste water and sludge Physical and physical-chemical parameters (group C) Part 3: Determination of spectral absorption in the UV range, spectral absorption coefficient (C 3)