

# Light scattering by small particles

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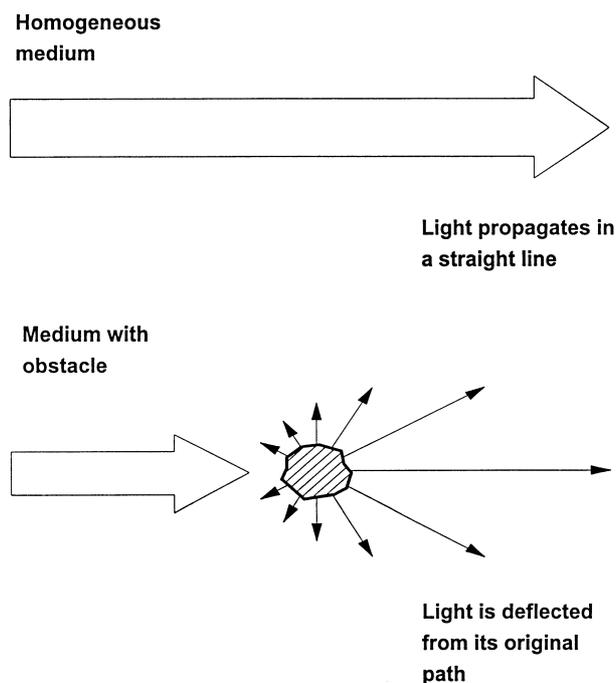
**ABSTRACT:** On-line turbidimeters are currently used for monitoring particle concentration in water and gas treatment processes. For small particle concentration, the intensity of scattered light is a linear function of the particle concentration, as long as a number of other parameters are kept constant: the refractive indexes of the particles and the surrounding medium, size, measuring angle and wavelength of the light. An international standard has been created in order to define the characteristics of the turbidimeters and the calibration suspension. The effects of the parameters are described and quantified. The special aspects of the measurement of very low turbidity values in water are treated: the zero value of water and the definition of the calibration conditions. A measuring method is presented which grants long-term stability without recalibration.

The first industrial application for on-line turbidimeters was the monitoring of beer filtration in breweries, which started about 50 years ago. In the meantime, turbidimeters have been used in very diversified fields such as dust measurements in stacks, visibility in road tunnels and filtration control in the chemical industry. However, their main application today is the monitoring of drinking water treatment plants: control of the flocculation process by measuring the variations in the raw water (rivers, lakes, ground-water, sources) and the resulting properties, sand filtration survey and final quality control.

## NOMENCLATURE

FNU	Abbreviation for 'Formazine Nephelometric Units'. Calibration unit in compliance with standard ISO 7027, based on a formazine solution.
Formazine	Internationally established turbidity standard for the calibration of turbidimeters. Produced with the recipe described in the standard ISO 7027 (Water quality — Determination of turbidity).
Scattering angle	Angle between the direction of observation and the axis of the transmitted light.
Stray light	Component of the inherent brightening effect, the quantity of scattered light produced by the optics, e.g. the glass parts of the flow cell, even if a medium is theoretically free of scattered light. The amount of instrument stray light is a measure of the turbidimeter's optical quality.
Ext	Extinction or absorbance. Magnitude of absorption, attenuation of the radiation in spectroscopy.

beam from its path (Fig. 1). This physical process is called scattering. It depends on the colour of the light and the nature of the particle, and of the surrounding medium. In the case of a suspension with many particles, the collective effect of the scattering processes create the overall visual impression of



**Fig. 1** Propagation of light in a vacuum and in the presence of an obstacle.

## INTRODUCTION

### What is turbidity?

In an optically homogeneous medium of constant refractive index, light keeps moving straight ahead. Any change in the optical properties caused by an obstacle will deflect the light

turbidity. Turbidity units, such as FNU, are applied in an effort to express this qualitative phenomenon quantitatively.

The intensity  $I_{sc}$  of the scattered light can be expressed as the following function of five variables

$$I_{sc} = I_{sc}(c, d, \theta, \lambda, n),$$

where  $c$  is the concentration,  $d$  the particle diameter,  $\theta$  the measuring angle,  $\lambda$  the wavelength of the light and  $n$  the refractive index of the particles relative to the surrounding medium (for non-spherical particles, shape parameters must be added). The calculation of this equation is part of scattering theory. For spherical particles, the theory of Gustav Mie [1] provides the general solution for any values of the parameters. The equation has a complex mathematical structure and can only be solved numerically, with satisfactory results coming from today's powerful computers.

One of these variables exhibits a very simple correlation: the scattering intensity is a linear function of the particle concentration. In turbidimeters, this correlation can be used to determine the concentration. This is possible under the condition that all other parameters remain unchanged during the measurement. However, under process conditions this might not always be the case and the variables must be studied separately. In the next chapter, the main features will be briefly summarised.

### Variables affecting light scattering

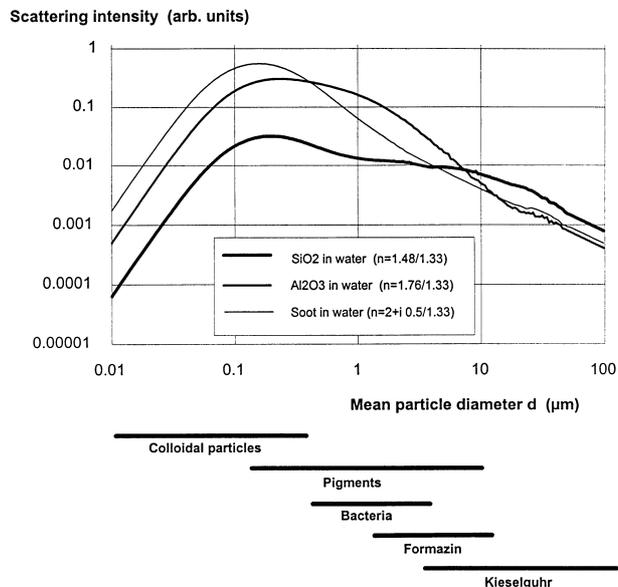
#### Concentration, $c$

In a suspension, each particle acts as the centre of an individual scattering process. If the particle concentration is low, such as in drinking water applications, these processes are independent of each other and only single scattering (scattering from single particles) must be considered. Consequently, the intensity of the scattered light is proportional to the concentration of the suspension. The validity of this law is widely recognized, and it constitutes the basis for turbidity measurement.

For higher particle concentration, e.g. very turbid liquids found in sewage plants, the instrument reading becomes larger or smaller than expected, depending on the type of measurement. This behaviour is caused by the effect of multiple scattering. In the case of a 5 cm flow cell, the influence of multiple scattering becomes apparent above 5 FNU.

#### Particle size, $d$

The intensity of the scattered light depends heavily on particle size. Figure 2 demonstrates the effect of mean particle diameter  $d$  for aqueous suspensions of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and soot. The overall shapes of the curves are similar for all these systems, although individual intensities differ considerably (materials with refractive indices closer to that of water scatter less light). With increasing particle diameter  $d$ , the intensity of the scattered light first increases in proportion to  $d^3$  (Rayleigh region), then passes a maximum around  $0.3 \mu\text{m}$ , and finally decreases

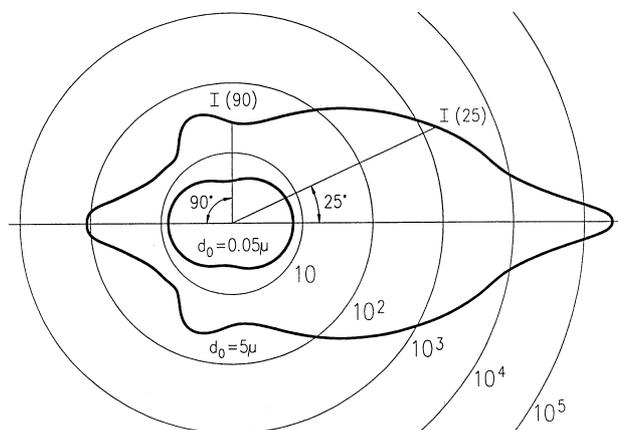


**Fig. 2** Intensity of scattered light as a function of mean particle size at constant mass concentration. Calculations for three materials in water were performed using the Mie [1] formalism (wavelength 550 nm, scattering angle  $90^\circ$ , lognormal particle size distribution with  $\sigma = 0.6$ , refractive index of water = 1.33). Also included are the size ranges of some typical particles.

steadily in proportion to  $1/d$  (diffraction region). The sizes of some typical particle species are included in this presentation, which demonstrates that the entire range between  $0.01 \mu\text{m}$  and  $100 \mu\text{m}$  should be considered.

#### Scattering angle, $\theta$

Figure 3 shows a polar plot of the scattering intensity. For large particles, forward scattering is dominant, whereas it is rather



**Fig. 3** Polar plot of the intensity of light scattered by  $\text{SiO}_2$  particles in water with mean diameters  $d = 0.05 \mu\text{m}$  and  $5 \mu\text{m}$  at a wavelength of 550 nm. The particle size distribution used for this calculation is quasi-Gaussian with  $\sigma 30\%$ . The total mass concentration is the same in both cases.

equally distributed for small particles. Thus, the ratio of the intensities at two angles (e.g. 25° and 90°) provides an indication of particle size.

*Wavelength, λ*

As a rule of thumb, the intensity of the scattered light decreases with increasing wavelength. This effect depends on particle size and is more pronounced for small particles. Below a diameter of 0.05 μm it can be expressed in terms of Rayleigh’s law  $1/\lambda^4$ , whereas for larger particles, the effect is less pronounced.

This is illustrated in Fig. 4. Calculated scattering intensities for particles with 0.05 μm, 0.25 μm and 0.6 μm diameters are plotted as a function of wavelength.

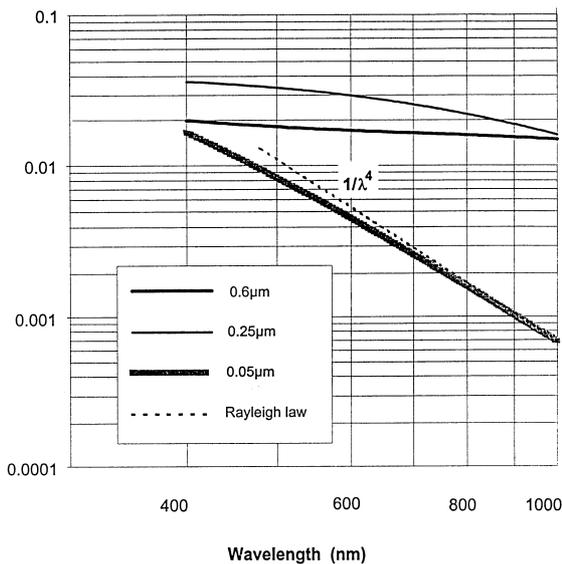
*Refractive index, n*

Scattering is also affected by the difference between the refractive indices of the particle and the medium: the smaller this difference, the lower the scattering intensity.

This can be shown in an experiment: SiO<sub>2</sub> particles ( $n = 1.47$ ) were dispersed in liquids with different refractive indices (methanol benzothiazole mixtures,  $n = 1.33$ – $1.64$ ) and the light scattering was measured. As Fig. 5 clearly shows, there is no scattering when the refractive index of the mixture and the particles match.

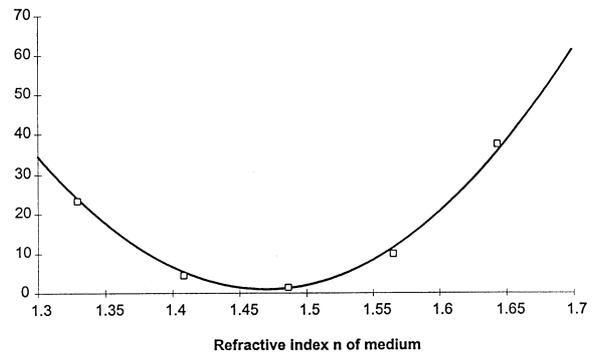
As a consequence, watery materials (such as biological cells), produce a relatively weak signal per particle compared with metal oxides.

Scattering intensity (arbitrary units)



**Fig. 4** Intensity of scattered light as a function of wavelength. Calculations for three particle diameters of SiO<sub>2</sub> in water were carried out using the Mie [1] formalism (wavelength 550 nm, scattering angle 90°, lognormal particle size distribution with  $\sigma = 0.6$ , refractive index of SiO<sub>2</sub>  $n = 1.47$  and of water  $n = 1.33$ ). The dashed line represents Rayleigh’s law  $1/\lambda^4$ , valid for very small particles.

Scattering intensity



**Fig. 5** Light scattering of SiO<sub>2</sub> suspended in methanol/benzothiazole mixtures with varying refractive indices (SiO<sub>2</sub> 1.47; methanol 1.33; benzothiazole 1.64). The line represents a quadratic fit around  $n = 1.47$ .

**Low turbidity levels in water**

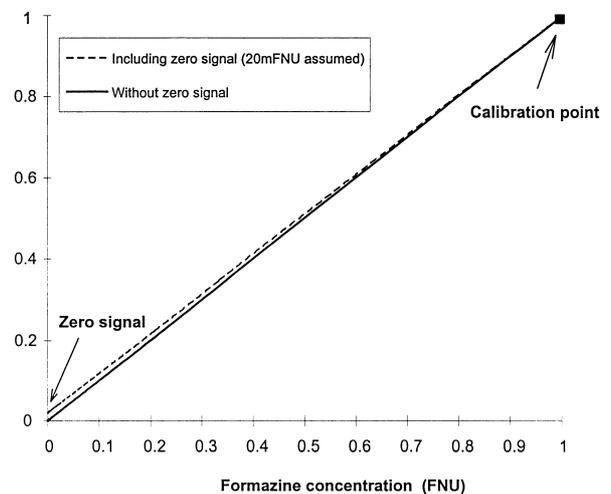
*Measurement of low turbidities*

Very roughly, values below 1 FNU may be treated as low turbidities. This is equivalent to about one-quarter of the turbidity level visible to the naked eye.

For an accurate measurement of low turbidities, the instrument reading at zero formazine concentration (i.e. for ‘pure’ water) is crucial. In the following this will be called the ‘zero signal’. In general, it will be below 0.1 FNU (100 mFNU) and has little effect on a high turbidity measurement. However, for low level measurements, it may well reach 10% of the full scale reading or more.

This situation is illustrated in Fig. 6. The plot shows the

Instrument reading (FNU)



**Fig. 6** Predicted reading of a turbidimeter in the presence of a zero signal (= offset signal at zero formazine concentration). The solid line shows what is expected from the calibration at 1 FNU; the dashed line includes the influence of the zero signal, which is assumed to be 20 mFNU.

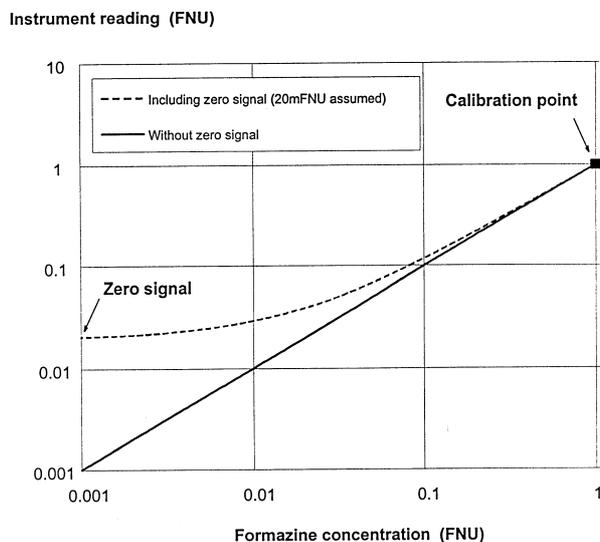


Fig. 7 Same as Fig. 9, but on a log-log scale.

reading of a hypothetical turbidimeter which has been correctly calibrated with formazine at full scale (1 FNU). The zero signal is assumed to be 20 mFNU. Obviously, the instrument does not reproduce the formazine concentrations correctly at the lower end of the scale. In order to represent the lower end of the scale more clearly, the curve in Fig. 6 is replotted on a double logarithmic scale in Fig. 7. Here, the situation appears even more pronounced.

It can therefore be concluded that for low turbidity measurements, the zero signal is an important parameter. Its minimum value is given by the material properties of the water. Higher zero signals are caused by either particles in the water or stray light in the instrument. These problems will be analysed in the following section.

#### The zero signal of turbidimeters

Ultra-fine turbidity measurements require low zero signals. Instrument stray light, as a source of zero signal, should be kept as small as possible. It is advisable to put great effort on optics and flow cell design. Alternatively, the zero signal could be electronically suppressed. This, however, has the disadvantage of reduced resolution and zero point stability. It is therefore recommended to observe the zero signal directly and check it against pure water. The question then arises: what is the turbidity of water?

The zero signal measured using filtered water is made up of these three components:

- 1 Scattering in pure H<sub>2</sub>O;
- 2 Scattering at particles which have passed the filter; and
- 3 Instrument stray light.

The first component is a constant of the material. Because of the thermal motion of the molecules, the liquid's density is not

uniform. The corresponding fluctuations in its optical properties can be interpreted as 'particles'. These 'particles' are very small and scatter light according to Rayleigh's law (see above). The effect is often called 'molecular scattering' although this term is somewhat misleading because scattering at a single molecule is not considered. If a reliable value for this physical constant is known, ultrafine turbidimeters can be checked independently.

The second component depends on the filtration quality of the water. A typical on-line filtration scheme is the following: pre-filtering for large particles and subsequent membrane filtering with 0.2  $\mu\text{m}$  pore width. Careful syringe filtration (avoiding exposure to ambient air) with a 0.05  $\mu\text{m}$  pore width does not further reduce turbidity. It is therefore assumed that on-line filtration with a pre-filter and subsequent 0.2  $\mu\text{m}$  membrane filtration yields water where the remaining particles are negligible or, at least, cannot be significantly reduced by further filtration.

The third component depends on the performance of the instrument. Under laboratory conditions, stray light levels below 0.5 mFNU can be achieved and checked experimentally.

Under these experimental conditions, the turbidity of pure water was determined as  $20 \pm 2$  mFNU at 550 nm ( $8 \pm 1$  mFNU at 860 nm). This value, which could not be reduced by further filtration, is only about 5–10% higher than that of synthetic fused silica, a material with an extremely low turbidity. This confirms the assumption that the water we used was virtually particle-free and that its turbidity was based on molecular scattering. This therefore becomes the physical constant (temperature influences are neglected) needed to check ultrafine turbidity instruments.

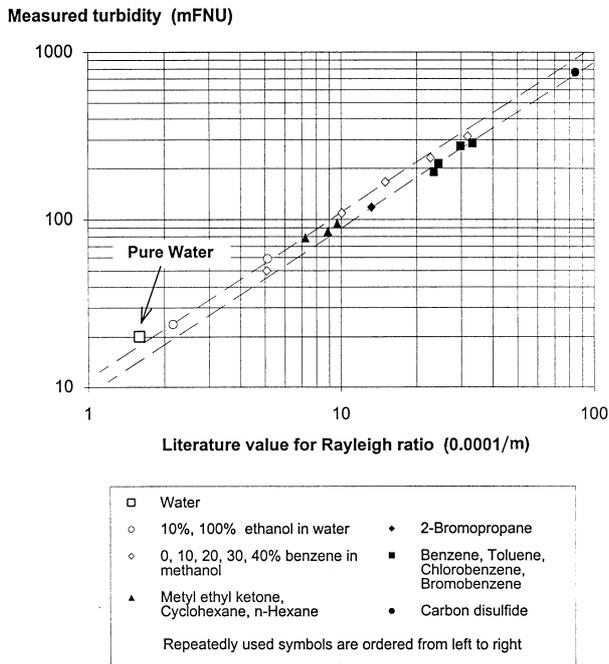
Further corroboration of the reliability of pure water turbidity comes from the following comparisons.

#### The Rayleigh ratio of the solvents

The Rayleigh ratio  $R_\theta$  is the energy scattered by a unit volume per unit solid angle in the direction  $\theta$ , when the medium is illuminated with unit intensity [2]. This quantity is often used for the study of liquids in physical chemistry and a great deal of data is available from the literature. In this case, the Rayleigh ratio at 90° can be compared directly with our turbidity measurements.

The turbidities of several pure chemicals were measured at 550 nm and compared with the corresponding Rayleigh ratios published by different authors [3–7; and P. Schurtenberger, Institute for Polymeres, ETH Zürich, personal communication]. The Rayleigh ratios are plotted on the horizontal axis of Fig. 8, the measured turbidities on the vertical axis. All points tend to be on a straight line which reflects a linear correlation between these quantities. Water, being the clearest liquid, follows the same trend. The data are quite consistent; the (slight) deviations may be caused by differences in the measurement methods used or by residual particles.

This again supports the assumption that the measured



**Fig. 8** Comparison of measured turbidities with literature values of the Rayleigh ratio of different solvents [3–7; and P. Schurtenburger, personal communication]. The wavelength is 550 nm. Every point corresponds to a solvent: the Rayleigh ratios are plotted on the x-axis, the measured turbidities on the y-axis. The graph shows the linear correlation between Rayleigh ratio and turbidity (the dashed lines represent the limits within which this statement is valid).

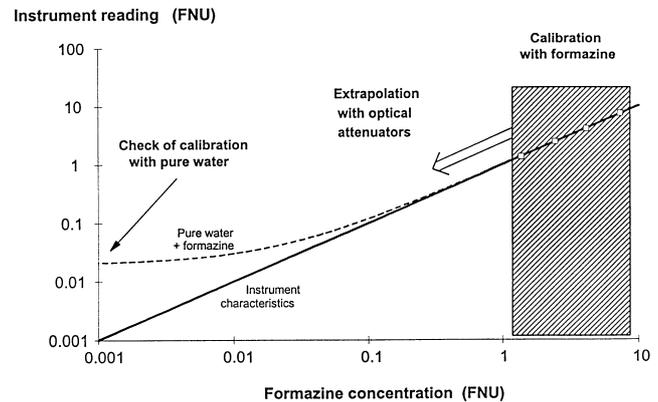
turbidity of water,  $20 \pm 2$  mFNU at 550 nm and  $8 \pm 1$  mFNU at 860 nm, is caused by molecular scattering and is thus a well-defined constant.

### Calibration and stability

Calibration is usually carried out with formazine. A few dilutions are sufficient for the adequate calibration of a single measuring range. Above 1 FNU, formazine calibration is very reliable and convenient.

Below 1 FNU, the dilution and handling of formazine become difficult. Great instrumental effort is necessary to obtain reliable and stable suspensions, but accuracies of  $\pm 10$  mFNU can be reached [8].

Another method is based on the exact linearity between scattering intensity and particle concentration (see above). The instrument is calibrated with formazine of a reasonably high concentration (e.g. 5 FNU). For the lower ranges, the light is optically (or electronically) attenuated in order to stimulate lower formazine turbidities. The optical attenuators can be accurately gauged externally. Figure 9 illustrates this method, which allows calibration down to a full scale range of



**Fig. 9** Calibration of an ultrafine turbidimeter using optical attenuation. Formazine calibration is done only in the shaded area, where concentrations are accurate. The attenuators were gauged independently. If calibration is correct, the reading of pure water will be 20 mFNU (at 550 nm).

100 mFNU (smaller ranges are not useful for water measurements). Instruments calibrated this way always measure the total amount of scattered light, including the light from molecular scattering in water. Consequently, for pure water, the instrument reading is  $20 \pm 2$  mFNU at 550 nm ( $8 \pm 1$  mFNU at 860 nm). This is the final check of the instrument: higher values indicate an incorrect calibration or, much more likely, stray light from the flow cell.

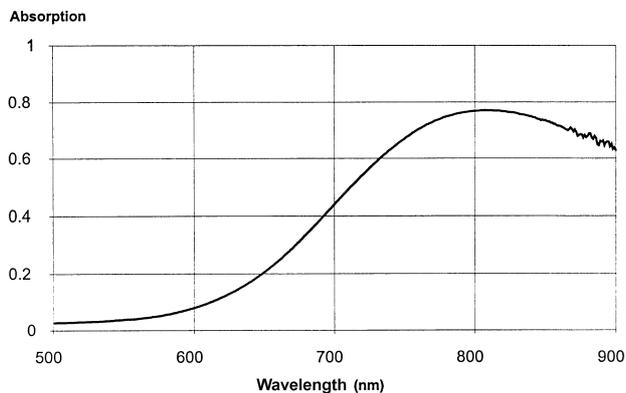
Stability is one of the most important features of an instrument. Especially in the case of turbidimeters, where flow cells often become contaminated, a periodic check is useful. For turbidities above 1 FNU this can be done with formazine. Alternatively, checking rods which have turbidities above or below 1 FNU, supplied by the manufacturer can be used. For the zero signal, the best test is pure filtered water, as described above.

### Measurement wavelength

The wavelength of the light is an important parameter for turbidity measurements. Basically, light with a defined, narrow-banded spectrum should be used (white light is less suited because of its inherent spectral uncertainty). Sensitivity to different types of particles varies strongly with wavelength. A simple rule says: small particles are best detected with short wavelengths. However, the ISO standard [9] prescribes 860 nm, with 550 nm mentioned in a footnote. In the following, some differences between these two wavelengths are presented.

#### *Dissolved material*

At 860 nm there is usually only weak absorption by the dissolved material. This is particularly important for instruments which are not colour compensated (i.e. the reference beam does not pass through the measuring cell). However,



**Fig. 10** Absorption spectrum of 1g/L  $\text{Cu}^{2+}$  ( $\text{CuSO}_4$ ) in water at a path-length of 4 cm.

860 nm does not replace colour compensation in every case; e.g.  $\text{CuSO}_4$  solutions (wastewaters from galvanic plants) absorb strongly at 860 nm and are practically transparent at 550 nm (see Fig. 10).

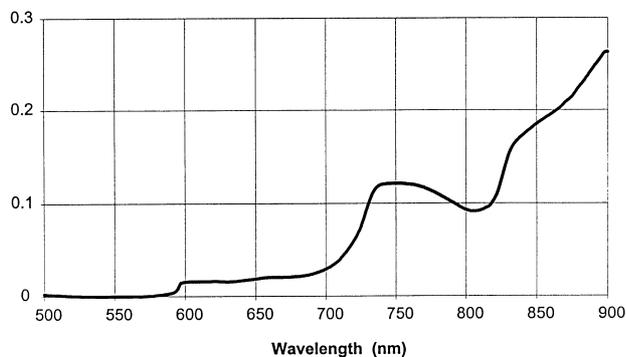
#### IR absorption of water

Water itself exhibits a significant absorption at 860 nm and is practically transparent at 550 nm (see Fig. 11). At 860 nm and for a 100 mm cell, the absorption is 0.2 Ext, corresponding to a transmission of 63%.

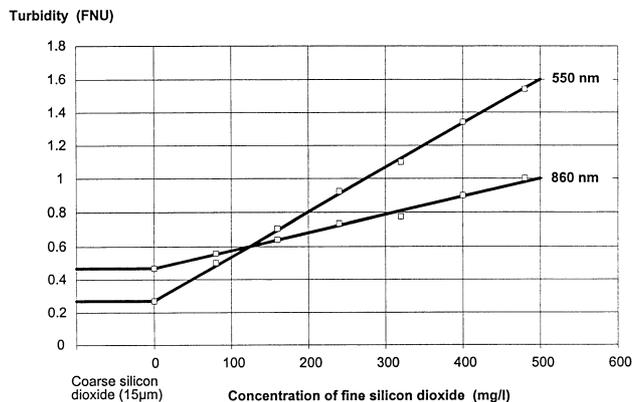
#### Sensitivity to small particles

For small particles below  $0.2 \mu\text{m}$  diameter the sensitivity is significantly higher at 550 nm than at 860 nm. Sensitivity tends to decrease with  $1/\lambda^4$ , i.e. following Rayleigh's law (see Fig. 4). This can be demonstrated with the following experiment (see Fig. 12): Two turbidimeters, one measuring at 550 nm and the other at 860 nm, both calibrated with formazine, are used. As the start of suspension, the large particle ( $15 \mu\text{m}$ ) kieselguhr (diatomaceous earth) is measured by both instruments. The readings are 0.27 FNU at 550 nm and 0.47 FNU at 860 nm (the

Absorption for 100mm cell (Ext)



**Fig. 11** Absorption spectrum of water.



**Fig. 12** Turbidity of a suspension of fine  $\text{SiO}_2$  particles as a function of concentration at 860 nm and 550 nm (instruments calibrated with formazine). Particle size of the fine  $\text{SiO}_2$  is below  $0.1 \mu\text{m}$ . Note: the starting suspension contains only large  $\text{SiO}_2$  particles; dosage of fine  $\text{SiO}_2$  begins at the abscissa value of 0.

readings are not equal because the instruments were not calibrated with kieselguhr). Now, very fine  $\text{SiO}_2$  particles (below  $0.1 \mu\text{m}$ ) are added in equal amounts. The corresponding increase in turbidity is monitored by both instruments: while at 550 nm a dosage of 100 mg/L  $\text{SiO}_2$  doubles the turbidity, at 860 nm it increases the turbidity only by 20%. In other words, the sensitivity to small particles is much higher at 550 nm.

#### Zero signal

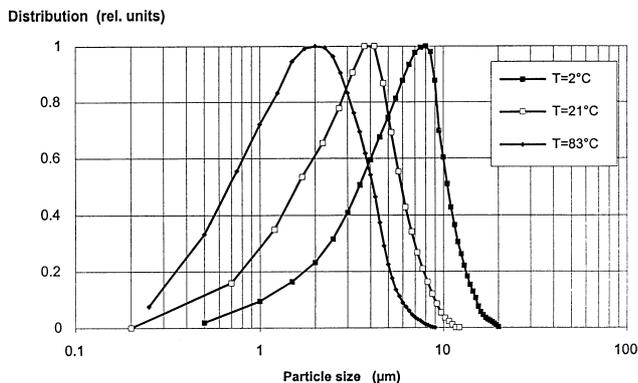
As mentioned above, the scattering intensity of pure water is greater at 550 nm than at 860 nm (20 and 8 mFNU, respectively). The instrument stray light is small, and roughly the same at both wavelengths ( $< 3$  mFNU for low turbidity flow cells). The zero signal in an 860 nm instrument is thus smaller than in a 550 nm instrument by a factor of about two. For measurements of large particles (such as kieselguhr or formazine), therefore, 860 nm is preferable. However, the sensitivity to small particles is also reduced (see above), which compensates the apparent advantage of the smaller zero signal at 860 nm.

#### Applications for measurements at two angles

Generally, the ratio  $\alpha$  between the intensities at  $25^\circ$  and  $90^\circ$  ( $\alpha = I_{25^\circ}/I_{90^\circ}$ ), increases strongly with particle size up to about  $1 \mu\text{m}$  (for larger particles  $\alpha$  may vary slightly in both directions, depending on particle type). Thus, an indication of particle size can be extracted from the angle of dependence of the scattered light. A few applications of this are given in the following.

#### Turbidity standards

Formazine is used as a turbidity standard. Since the intensity of the scattered light depends on the particle size, a constant and reproducible size distribution is crucial. This is guaranteed by



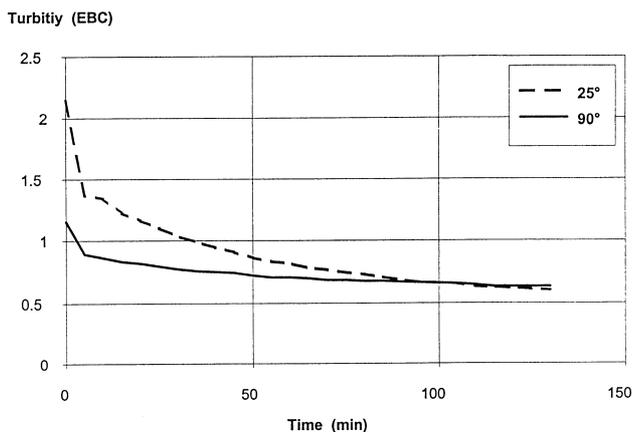
**Fig. 13** Measured particle size distribution of formazine produced at three different formation temperatures.

the chemical process in formazine formation. However, if these processes have not been performed under the correct conditions, or if the formazine has been stored for a long period of time, its size distribution changes.

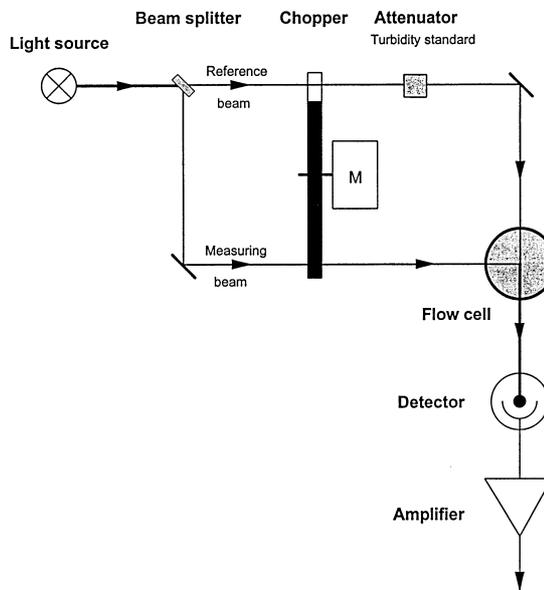
As an example, particle size distributions in formazine suspensions formed at different temperatures are plotted in Fig. 13: when the formazine reaction takes place at lower temperatures, the mean particle size is increased. These differences are not visible to the naked eye, but affect the accuracy of the standard.

*Filtration of beer*

Figure 14 shows the decrease in the turbidity of beer during an experimental closed loop filtration. Because larger particles are filtered more efficiently, the 25° turbidity decreases faster and finally falls to below the 90° turbidity. The ratio of the turbidities can be used to maintain the filtration quality [10].



**Fig. 14** Turbidity of beer during filtration as a function of time [9].



**Fig. 15** On-line turbidity monitor measuring at 90°.

**Instrumentation**

*Continuous measurement*

The basic requirement of continuous measurement is long-term stability. This can be achieved easily with a dual beam photometer (see Fig. 15). The light is split into a measuring and a reference beam using a beam splitter and a chopper. Both beams are emitted from the same lamp and strike the same detector. A reading is obtained by the ratio of intensity of the two beams. Since both beams lose the same amount of intensity when the lamp or detector ages, these changes have no effect.

*Colour compensation*

The principle of colour compensation is carried out by both beams passing through the cell (see Fig. 15). While the scattered light is taken at 90° from the incident measuring beam, the reference beam goes straight through the cell. Both paths have the same length, and the colour of the sample absorbs the same quantity of light in both beams. So at reasonable concentrations, colour is compensated at any wavelength.

*Flow cell and zero signal*

For particle-free water, the zero signal consists of molecular scattering, which is a constant (20 mFNU at 550 nm and 8 mFNU at 860 nm), and the instrument stray light. Generally, the stray light depends on the type of flow cell used, as well as the contamination of its windows (usually between 3 and 30 mFNU).

In the case of a high particle concentration, or where regular window cleaning is impossible, instruments with windowless

cells can be used. Here, the water passes through the light beam as a free-falling jet.

## CONCLUSIONS

For measurements of very low turbidities (200 mFNU and below), the zero signal of the instrument limits sensitivity. This signal should be kept as low as possible, and an independent check should be available.

Formazine is not recommended for very low turbidities, because it cannot be produced with sufficient accuracy. As an alternative, the molecular scattering of pure water can be used as a reliable standard. Molecular scattering is a material property that allows an accurate check of the instrument zero signal: the turbidity of pure water is  $20 \pm 2$  mFNU at 550 nm and  $8 \pm 1$  mFNU at 860 nm.

According to ISO 7027, turbidity should be measured at 860 nm (550 nm is mentioned in a footnote). However, these two wavelengths do not have the same sensitivity to different sizes of particles. If a high sensitivity to very small particles is of primary interest, 550 nm is preferable, in spite of the standard.

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