

TURBIDITY SCIENCE

Technical Information Series—Booklet No. 11

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In memory of
Clifford C. Hach
(1919-1990)

inventor, mentor, leader and, foremost,
dedicated chemist

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I. Introduction and Definition

An important water quality indicator for almost any use is the presence of dispersed, suspended solids—particles not in true solution and often including silt, clay, algae and other microorganisms, organic matter and other minute particles. The extent to which suspended solids can be tolerated varies widely, as do the levels at which they exist. Industrial cooling water, for example, can tolerate relatively high levels of suspended solids without significant problems. In modern high pressure boilers, however, water must be virtually free of all impurities. Solids in drinking water can support growth of harmful microorganisms and reduce effectiveness of chlorination, resulting in health hazards. In almost all water supplies, high levels of suspended matter are unacceptable for aesthetic reasons and can interfere with chemical and biological tests.

Suspended solids obstruct the transmittance of light through a water sample and impart a qualitative characteristic, known as turbidity, to water. The American Public Health Association (APHA) defines turbidity as an “expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample.”¹ Turbidity can be interpreted as a measure of the relative clarity of water. Turbidity is not a direct measure of suspended particles in water but, instead, a measure of the scattering effect such particles have on light.

Theory of Light Scattering

Very simply, the optical property expressed as turbidity is the interaction between light and suspended particles in water. A directed beam of light remains relatively undisturbed when transmitted through absolutely pure water, but even the molecules in a pure fluid will scatter light to a certain degree. Therefore, no solution will have a zero turbidity. In samples containing suspended solids, the manner in which the sample interferes with light transmittance is related to the size, shape and composition of the particles in the solution and to the wavelength (color) of the incident light.

A minute particle interacts with incident light by absorbing the light energy and then, as if a point light source itself, re-radiating the light energy in all directions. This omnidirectional re-radiation constitutes the “scattering” of the incident light. The spatial distribution of scattered light depends on the ratio of particle size to wavelength of incident light. Particles much smaller than the wavelength of incident light exhibit a fairly symmetrical scattering distribution with approximately equal amounts of light scattered both forward and backward (*Figure 1A*). As particle sizes increase in relation to wavelength, light scattered from different points of the sample particle create interference patterns that are additive in the forward direction. This

¹ *Standard Methods for the Examination of Water and Wastewater*, published by APHA, AWWA and WPCF, 17th edition, 1989, pages 2-12.

constructive interference results in forward-scattered light of a higher intensity than light scattered in other directions (*Figures 1B and 1C*). In addition, smaller particles scatter shorter (blue) wavelengths more intensely while having little effect on longer (red) wavelengths. Conversely, larger particles scatter long wavelengths more readily than they scatter short wavelengths of light.

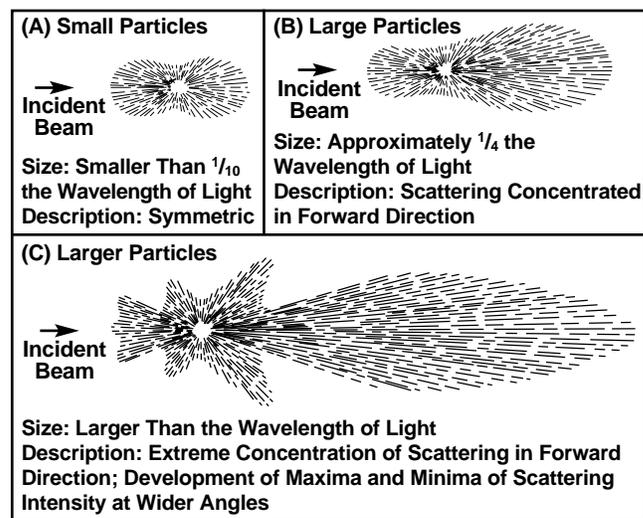


Figure 1. Angular patterns of scattered intensity from particles of three sizes. (A) small particles, (B) large particles, (C) larger particles. From Brumberger, et al, “Light Scattering,” *Science and Technology*, November, 1968, page 38.

Particle shape and refractive index also affect scatter distribution and intensity. Spherical particles exhibit a larger forward-to-back scatter ratio than coiled or rod-shaped particles. The refractive index of a particle is a measure of how it redirects light passing through it from another medium such as the suspending fluid. The particle’s refractive index must be different than the refractive index of the sample fluid in order for scattering to occur. As the difference between the refractive indices of suspended particle and suspending fluid increases, scattering becomes more intense.

The color of suspended solids and sample fluid are significant in scattered-light detection. A colored substance absorbs light energy in certain bands of the visible spectrum, changing the character of both transmitted light and scattered light and preventing a certain portion of the scattered light from reaching the detection system.

Light scattering intensifies as particle concentration increases. But as scattered light strikes more and more particles, multiple scattering occurs and absorption of light increases. When particulate concentration exceeds a certain point, detectable levels of both scattered and transmitted light drop rapidly, marking the upper limit of measurable turbidity. Decreasing the path length of light through the sample reduces the number of particles

between the light source and the light detector and extends the upper limit of turbidity measurement.

History

Practical attempts to quantify turbidity date to 1900 when Whipple and Jackson² developed a standard suspension fluid using 1000 parts per million (ppm) of diatomaceous earth in distilled water. Dilution of this reference suspension resulted in a series of standard suspensions used to derive a ppm-silica scale for calibrating contemporary turbidimeters.

Jackson applied the ppm-silica scale to an existing turbidimeter called a diaphanometer, creating what became known as the Jackson Candle Turbidimeter. Consisting of a special candle and a flat-bottomed glass tube, this turbidimeter was calibrated by Jackson in graduations equivalent to ppm of suspended silica turbidity. Measurement was made by slowly pouring a turbid sample into the tube until the visual image of the candle flame, viewed from the open top of the tube, diffused to a uniform glow (Figure 2). Visual image extinction occurred when the intensity of the scattered light equaled that of transmitted light. The depth of the sample in the tube was then read against the ppm-silica scale, and turbidity was referred to in terms of Jackson turbidity units (JTU). However, standards were prepared from materials found in nature, such as Fuller's earth, kaolin and stream-bed sediment, making consistency in formulation difficult to achieve.

Turbidity Standards

In 1926, Kingsbury and Clark³ developed formazin, an almost ideal suspension for turbidity standards prepared by accurately weighing and dissolving 5.00 g of hydrazine sulfate and 50.0 g of hexamethylenetetramine in one liter of distilled water (Figure 3). The solution develops a white turbidity after standing at 25 °C for

²M.I.T. Quarterly, vol. 13, 1900, page 274.

³Kingsbury, Clark, Williams and Post, J. Lab. Clin. Med., Vol. 11, 1926, page 981.

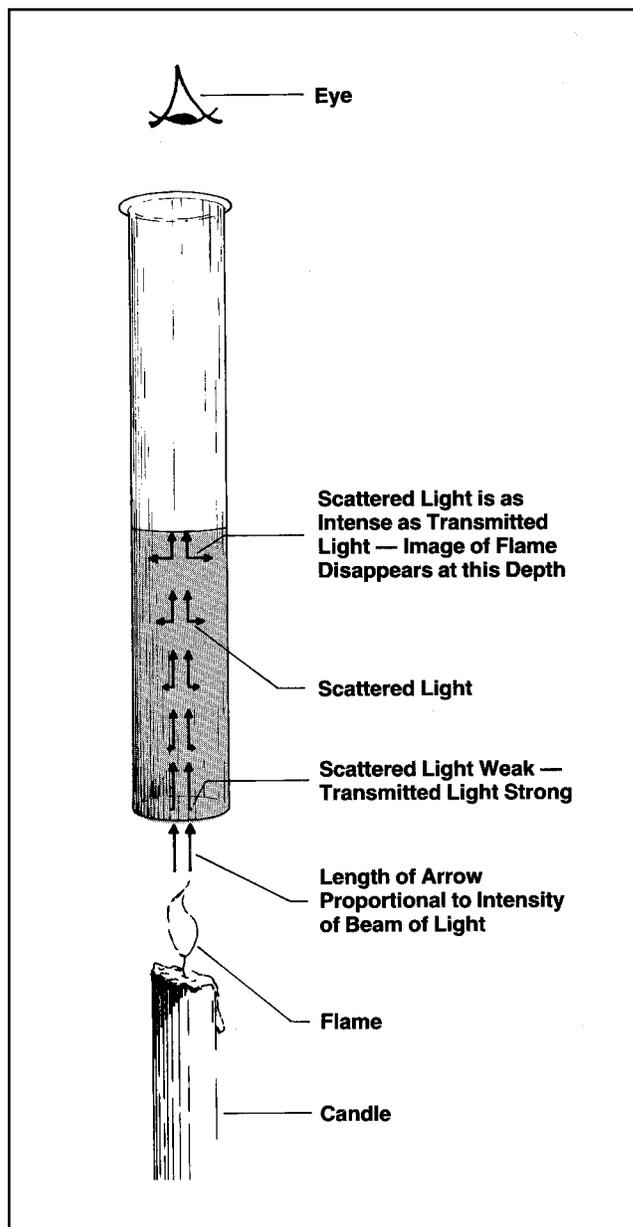


Figure 2. Jackson Candle Turbidimeter.

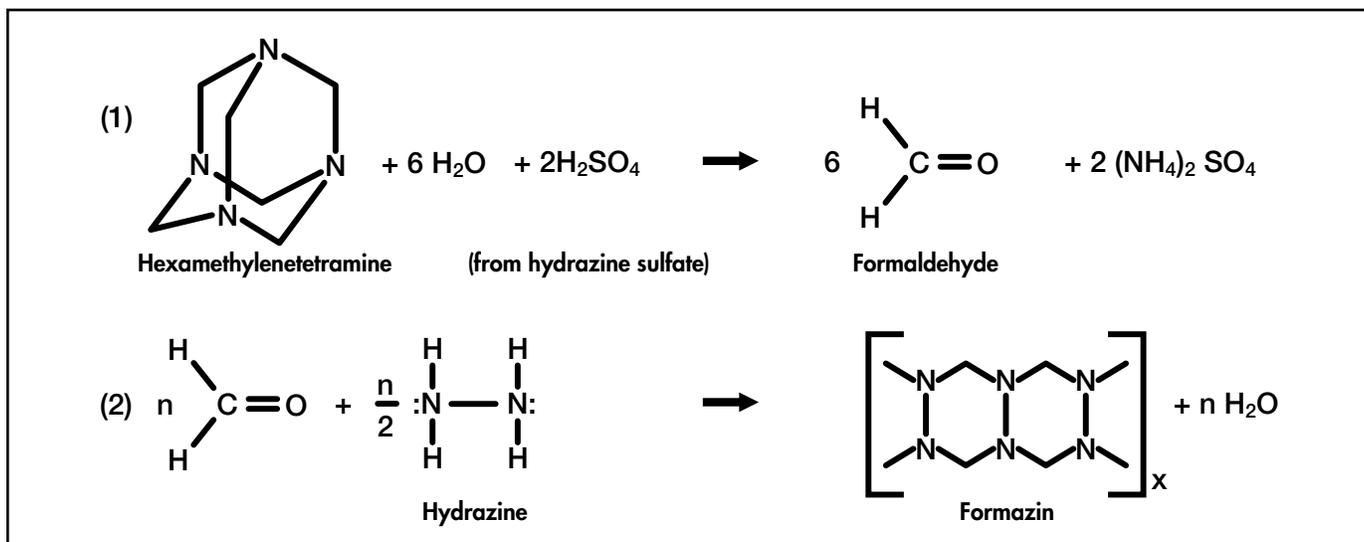


Figure 3. Synthesis of formazin.

48 hours. Under ideal environmental conditions of temperature and light, this formulation can be prepared repeatedly with an accuracy of $\pm 1\%$. Formazin is the only known turbidity standard that can be repeatedly made from traceable raw materials. All other standards, both alternate and secondary, must be controlled against formazin. Primary turbidity standards prepared by direct synthesis of formazin suspensions have been accepted almost universally by the water industry and other associated industries.

Formazin has several desirable characteristics that make it an excellent turbidity standard. First, it can be reproducibly prepared from assayed raw materials. Second, the physical characteristics make it a desirable light-scatter calibration standard. The formazin polymer consists of chains of several different lengths, which fold into random configurations. This results in a wide array of particle shapes and sizes ranging from less than 0.1 to over 10 microns. Studies of the particle distribution indicate irregular distributions among different lots of standards, but the overall statistical nephelometric scatter is very reproducible. This wide array of particle sizes and shapes analytically fits the wide possibility of particle sizes that are found in real-world samples. Due to the statistical reproducibility of the nephelometric scatter of white light by the formazin polymer, instruments with traditional tungsten filament white light optical designs can be calibrated with a high degree of accuracy and reproducibility. The randomness of particle shapes and sizes within formazin standards yields statistically reproducible scatter on all makes and models of turbidimeters. Due to formazin's reproducibility, scattering characteristics and traceability, turbidimeter calibration algorithms and performance criteria should be universally based on this standard.

In 1955, the relationship of parts per million silica concentration and turbidity had been abandoned and the 10th and subsequent editions of *Standard Methods* described turbidity in terms of light scattering due to suspended matter. The terms "ppm units" and "silica scale" were discontinued; units adopted were simply "turbidity units." When formazin was accepted as the primary reference standard, units of turbidity measurement became known as formazin turbidity units (FTU). Formazin was first adopted by the APHA and American Water Works Association (AWWA) as the primary turbidity standard material in the 13th edition of *Standard Methods for the Examination of Water and Wastewater*. The USEPA defines primary standards slightly differently, using the term to mean standards that USEPA has determined can be used for reporting purposes.

The subject of standards in turbidimetric measurement is complicated partly by the variety of types of standards in common use, and partly by the differences in definition used by organizations such as the USEPA and by APHA and AWWA in *Standard Methods*.

In the 19th edition of *Standard Methods*, clarification was made in defining primary and secondary standards. *Standard Methods* defines a primary standard as one that is prepared by the user from traceable raw materials, using precise methodologies under controlled environmental conditions. In turbidity, the only standard that can be strictly defined as primary is formazin that has been prepared by the user on the bench.

Standard Methods now defines secondary standards as those standards a manufacturer (or an independent testing organization) has certified to give instrument calibration results equivalent (within certain limits) to those obtained when an instrument is calibrated with user-prepared formazin standards. Various secondary standards available for calibration include commercial stock suspensions of 4000 NTU formazin, stabilized formazin suspensions, and commercial suspensions of microspheres of styrene divinylbenzene copolymer.

Calibration verification "standards" supplied by instrument manufacturers, such as sealed sample cells filled with latex suspension or with metal oxide particles in a polymer gel, are used to verify instrument performance between calibrations and are not to be used in performing instrument calibrations.

If there is a discrepancy in the accuracy of a standard or an instrument, the primary standard (i. e. user-prepared formazin) is to be used to govern the validity of the issue. In turbidity, formazin is the only recognized true primary standard and all other standards are traced back to formazin.

USEPA definitions differ from those in *Standard Methods*. Currently, the USEPA designates user-prepared formazin, commercial stock formazin suspensions, stabilized formazin suspensions (StablCal™) and commercial styrene divinylbenzene suspensions (sometimes referred to as "alternative standards") as primary calibration standards and usable for reporting purposes. The term secondary is used by the USEPA for those "standards" that are used only to check or verify calibrations. Under this definition, primary does not have anything to do with traceability, only to acceptability for USEPA reporting purposes. This usage depends on the design of the standard.

Under the USEPA definition, secondary standards, once their values are determined versus primary formazin, are used to verify the calibration of a turbidimeter. However, these standards are not to be used for calibrating instruments. Examples of these standards include the metal oxide gels, latex suspensions, and any non-aqueous standards that are designed to monitor calibrations on a day-to-day basis.

StablCal™ Stabilized Formazin Turbidity Standards

A relatively new turbidity standard has been developed for use in calibrating or verifying the performance of any turbidimeter. StablCal™ Turbidity Standards contain the same light scattering polymer as traditional formazin primary turbidity standards. By using a different matrix, the formazin polymer in StablCal™ Standards is stabilized, and will not deteriorate over time as is the case with traditional low turbidity formazin standards. Due to this enhanced stability, StablCal™ Standards of any concentration ranging up to 4000 NTU can be manufactured and packaged in ready-to-use formats.

StablCal™ Turbidity Standards have many advantages over traditional formazin and other secondary turbidity standards. First, StablCal™ Standards are stable for a minimum of two years. *Figure 5 (p. 8)* displays the stability of StablCal™ Standards of three different concentrations — 2.0, 10.0, and 20.0 NTU. The stability of these standards is independent of concentration. Second, StablCal™ Standards are prepared at specific concentrations, eliminating the tedious and technique-sensitive preparation through volumetric dilutions. Third, StablCal™ Standards have the same particle size distribution as formazin and they can be directly substituted for formazin. Thus a StablCal™ Standard has a defined concentration that is independent of any instrumentation. *Figure 6 (p. 8)* demonstrates this comparable performance of the StablCal™ Standards to traditional formazin standards in the 1 to 5 NTU range on a wide array of turbidimeters. Last, StablCal™ Standards can be repeatably prepared from traceable raw materials, and can be considered primary standards.

The nature of the matrix of StablCal™ Standards has also helped to reduce the potential health risks that are associated with traditional formazin standards. Components in this matrix effectively scavenge any trace hydrazine from the standard. The hydrazine concentration is reduced to levels that are below analytical detection limits. Hydrazine levels in StablCal™ Standards have been reduced by at least three orders of magnitude over those in traditional formazin standards of equal turbidity.

Since the StablCal™ Standards are pre-made, the only user preparation required is to thoroughly mix the standards before use. This eliminates exposure to the standard, reduces potential to contaminate the standard, and saves time that would otherwise be spent in preparing these standards by volumetric dilution.

Nephelometry

Historically, the need for precise measurements of very low turbidity in samples containing fine solids demanded advancements in turbidimeter performance. The Jackson Candle Turbidimeter presented serious practical limitations because it could not measure turbidity lower than 25 JTU, was somewhat cumbersome, and was dependent on human judgment to determine the exact

extinction point. In addition, because the light source in the Jackson instrument was a candle flame, incident light emitted was in the longer wavelength end of the visible spectrum (yellow-red) where wavelengths are not scattered as effectively by small particles. For this reason, the instrument was not sensitive to very fine particle suspensions. (Very fine silica will not produce a flame image extinction in a Jackson Candle Turbidimeter.) The Jackson Candle Turbidimeter was also incapable of measuring turbidity due to black particles such as charcoal because light absorption was so much greater than light scattering that the field of view became dark before enough sample could be poured into the tube to reach an image extinction point.

Several visual extinction turbidimeters were developed with improved light sources and comparison techniques, but human judgment errors contributed to a lack of precision. Photoelectric detectors, sensitive to very small changes in light intensity, became popular to measure the attenuation of transmitted light through a fixed-volume sample. The instruments provided much better precision under certain conditions, but still were limited in their ability to measure high or extremely low turbidity. At low scattering intensities, the change in transmitted light, viewed from a coincident view, was so small that it is virtually undetectable by any means. Typically, the signal was lost in the electronic noise. At higher concentrations, multiple scattering interfered with direct scattering.

The solution to this problem was to measure the light scattered at an angle to the incident light beam and then relate this angle-scattered light to the sample's actual turbidity. A detection angle of 90° is considered to be very sensitive to particle scatter. Most modern instruments measure 90° scatter (*Figure 4*); these instruments are called nephelometers, or nephelometric turbidimeters, to distinguish them from generic turbidimeters, which measure the ratio of transmitted to absorbed light.

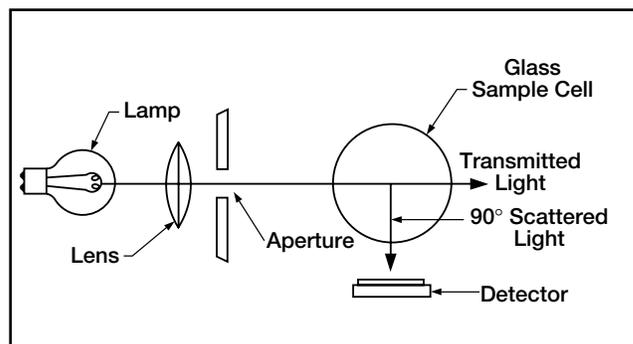


Figure 4. In nephelometric measurement, turbidity is determined by the light scattered at an angle of 90° from the incident beam.

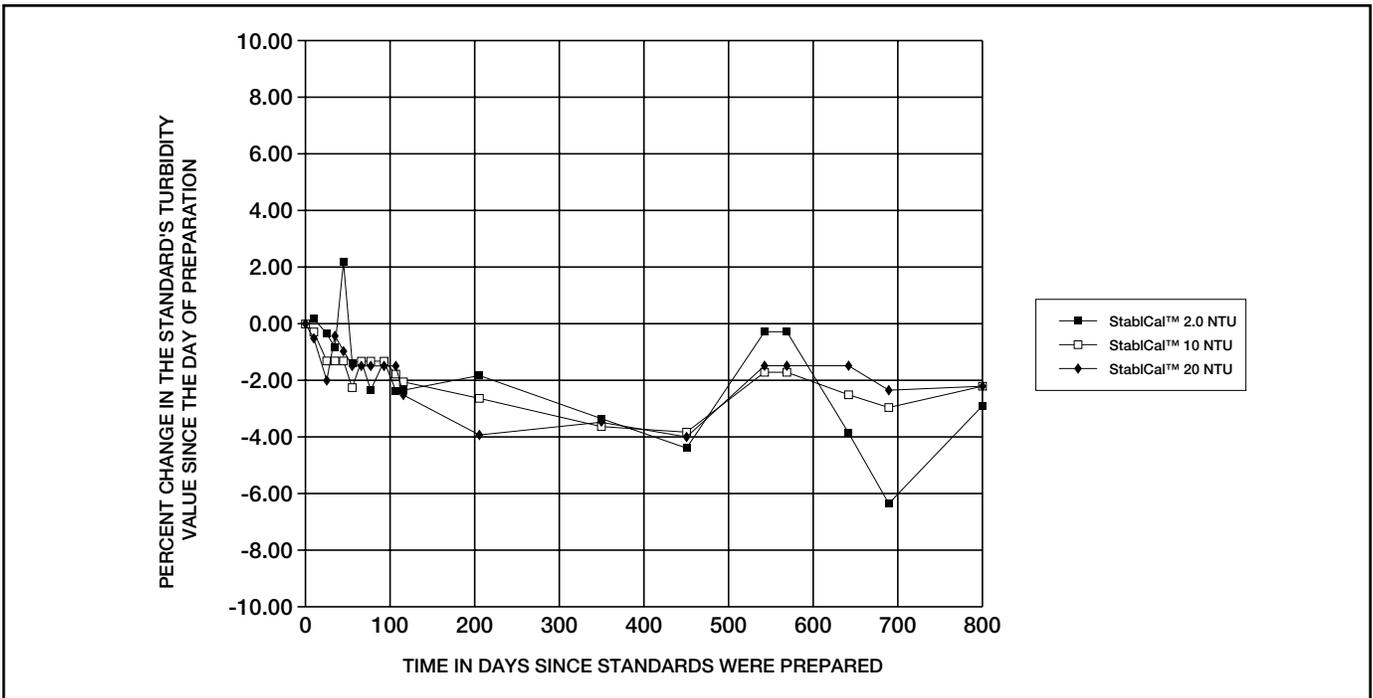


Figure 5. StabiCal™ Stabilized Formazin Standards—stability of standards over time.

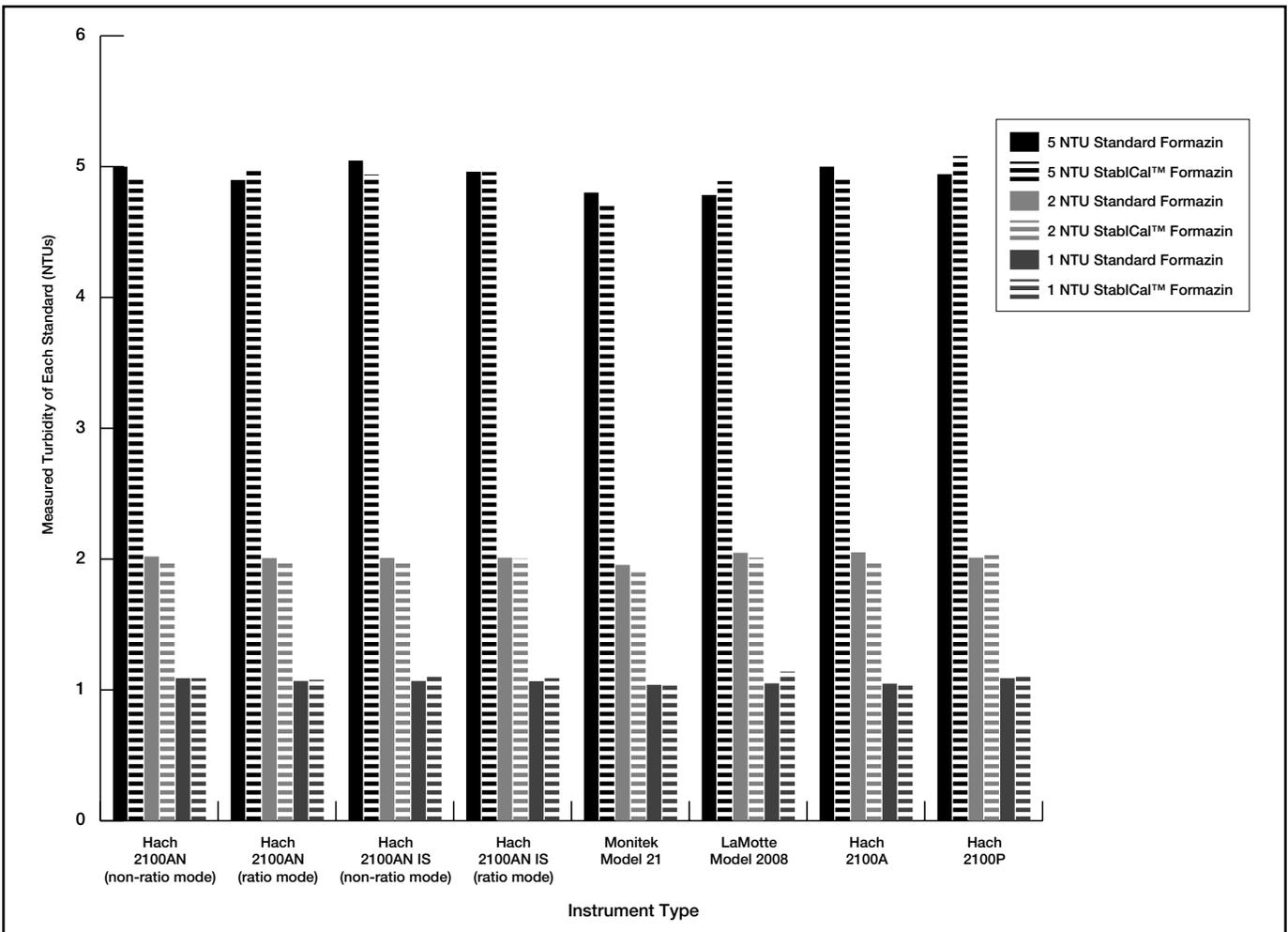


Figure 6. StabiCal™ Stabilized Formazin Standards versus dilute formazin. All instruments were calibrated with standard formazin.

Because of nephelometry's sensitivity, precision and applicability over a wide particle size and concentration range, the nephelometer has been adopted by *Standard Methods* as the preferred means for measuring turbidity. Likewise, the preferred expression of turbidity is in nephelometric turbidity units (NTU). The U.S. Environmental Protection Agency's publication, *Methods for Chemical Analysis of Water and Wastes*, also specifies the nephelometric method of analysis for turbidity measurement.

To distinguish between turbidity derived from the nephelometer and visual methods, results from the former are expressed as NTUs and from the latter as JTUs (1 JTU = 4 NTU's). In addition, the terms FNU (formazin nephelometric unit) and FAU (formazin attenuation unit) are used. FNU is a unit that applies to nephelometric measurement and FAU refers to a transmitted (or absorbed) measurement. However, NTUs, FTUs, FNUs and FAUs are all based on the same formazin primary standard.

II. Modern Instruments

Today, many methods exist for the determination of water contaminants, yet turbidity measurement is still important because it is a simple and undeniable indicator of water quality change. A sudden change in turbidity may indicate an additional pollution source (biological, organic or inorganic) or may signal a problem in the water treatment process.

Modern instruments are required to measure both extremely high and extremely low turbidity levels over an extreme range of sample particulate sizes and composition. An instrument's capability to measure a wide turbidity range is dependent on the instrument's design. The following sections discuss three critical design components of a nephelometer (the light source, scattered light detector and optical geometry), and how differences in these components affect an instrument's turbidimetric measurement. Most measurements are in the range or 1 NTU and lower. This requires instrument stability, low stray light, and excellent sensitivity.

Light Sources

While many types of light sources are used today in nephelometers, the most common is the tungsten-filament lamp. A lamp of this type has a wide spectral output and is rugged, inexpensive and dependable. Specific lamp output is often quantified in terms of the lamp's "color temperature" — the temperature at which a perfect "black body radiator" must be operated to produce a certain color. An incandescent lamp's color temperature and, therefore, spectral output is a function of the lamp's operating voltage. Stable incandescent lamp output requires a well-regulated power supply.

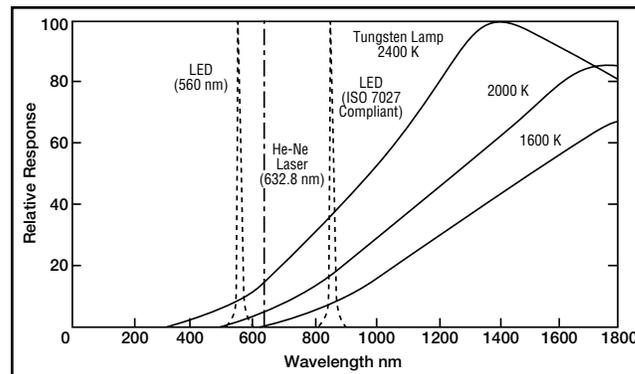


Figure 7. Typical spectral characteristics for a tungsten filament lamp at three color temperatures, a 560-nm light emitting diode, a He/Ne laser, and an 860 nm ISO 7027 compliant LED.

Monochromatic or narrow band sources can be used for nephelometric applications when specific particle types are present in the sample or when a well-characterized light source is necessary. An example of such a light source is the light emitting diode (LED). LEDs emit light in a narrow band compared to an incandescent source (*Figure 7*). Because they are more efficient than incandescent lamps at producing visible light, their power requirements for a given intensity are much lower. Application of these narrow band light sources is expanding. Other light sources less frequently used in nephelometric instrumentation include lasers, mercury lamps (discharge lamps) and various lamp/filter combinations.

For reporting purposes, the EPA requires the use of an instrument with a tungsten-filament lamp operated at a color temperature in the range of 2200 to 3000 °K. In the European Community, the ISO light requirement is an instrument with an incident light output of 860 nm and a spectral bandwidth of less than 60 nm. Tungsten light sources are more sensitive to small particles but sample color typically interferes; instruments with an 860 nm output are not as sensitive to small particles but are not likely to have color interference.

Detectors

When the imposed light signal has interacted with the sample, its response must then be detected by the instrument. There are four types of detectors presently used in nephelometers: the photomultiplier tube, the vacuum photodiode, the silicon photodiode, and the cadmium sulfide photoconductor.

These detectors differ in their response to a particular wavelength distribution (*Figure 8*). Photomultipliers used in nephelometric instrumentation have peak spectral sensitivity in the near ultraviolet and blue end of the visible spectrum. To maintain good stability, they require a well-regulated high voltage power supply. A vacuum photodiode generally exhibits a spectral response similar to that of a photomultiplier and is somewhat more stable than the photomultiplier.

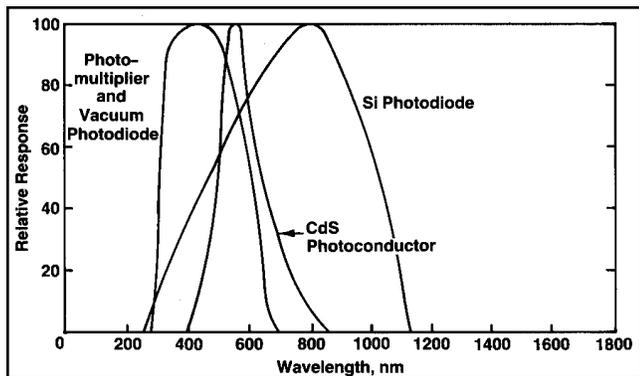


Figure 8. Typical spectral response characteristics of four photodetectors.

However, its characteristics are affected by environmental conditions, particularly humidity.

Silicon photodiodes generally have a peak spectral sensitivity in the visible red region or the near infrared. The cadmium sulfide photoconductor has a peak spectral response somewhere between that of the photomultiplier and the silicon photodiode.

Both the spectral distribution of the source and the spectral response of the detector are key elements in the performance of a nephelometer. Generally, for a given detector, when the incident light source is shorter in wavelength, the instrument is more sensitive to smaller particles. Conversely, when the light source is longer in wavelength, the instrument is more sensitive to relatively larger particles. An instrument's detector affects response in a similar way. Because photomultiplier and vacuum photodiode tubes are extremely sensitive in the ultraviolet and blue (short wavelength) regions of the spectrum, a nephelometer using a polychromatic light source and these detection components is more sensitive to relatively small particles. A silicon photodiode detector peaks in spectral response at longer wavelengths and is more sensitive to relatively larger particles.

In an actual instrument, the source/detector combination defines the effective spectral characteristics of the instrument and the manner in which it will respond to a sample. *Figure 9* depicts the spectral characteristics of an instrument with a tungsten light source and a cadmium sulfide photodetector. This instrument peaks in spectral sensitivity at approximately 575 nm. *Figure 10* shows the spectral characteristics of an instrument using the same light source and a silicon photodiode as the detector; its peak spectral sensitivity is approximately 875 nm. Because of this difference in spectral response, the instrument represented in *Figure 9* is more sensitive to smaller particles than the instrument depicted in *Figure 10*. These diagrams also illustrate that maximum efficiency of the system is obtained when the source and detector are well-matched and their spectral curves have maximum overlap.

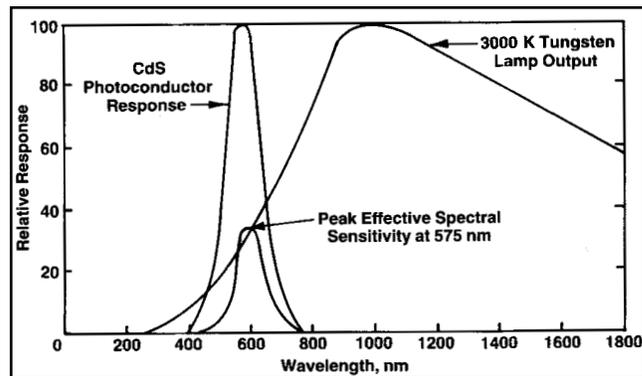


Figure 9. Effective spectral distribution for 3000 °K tungsten source/CdS photoconductivity detector system.

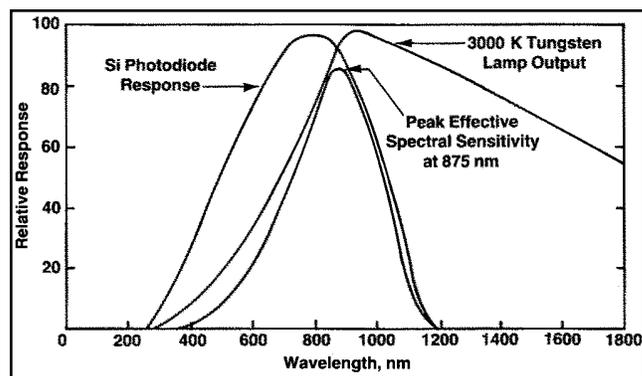


Figure 10. Effective spectral distribution for 3000 °K tungsten source/Si photodiode detector system.

Optical Geometry

The third critical component affecting the characteristic response of a nephelometer is the optical geometry, which incorporates instrument design parameters such as the angle of scattered light detection. As explained in the section dealing with scatter theory, differences in the make-up of sample particles cause different angular scattering intensities. Almost all nephelometers used in water and wastewater analysis use a 90° detection angle. In addition to being less sensitive to variations in particle size, a 90° detection angle affords a simple optical system with very low stray light.

The path length traversed by scattered light is a design parameter affecting both instrument sensitivity and linearity. Sensitivity increases as path length increases, but linearity is sacrificed at high particle concentrations due to multiple scattering and absorbance. Conversely, if the path length is decreased, the linearity range is increased but sensitivity is lost at low concentrations (this trade-off can be eliminated with an adjustable path length). The use of a short path length can also increase the impact of stray light. The EPA and ISO both require a path length of less than 10 cm total (measured from lamp filament to detector) in instrument design.

The ratio™ turbidimeters manufactured by HACH use a combination of optical devices to achieve a higher degree of stability: a 90° detector, a combination of transmitted, forward-scatter, and back-scatter detectors, and black mirrors. More information on these instruments and their components is provided in the ratio™ section of this booklet (see page 16).

III. Practical Aspects of Turbidity Measurement

Concepts explained in the previous section are basic to the fine accuracy achieved today when measuring turbidity under ideal conditions. In practical applications, however, significant problems can introduce interference and errors that reduce the accuracy of any instrument. To ensure the instrument is operating properly and providing the most accurate answers possible, it is important to verify its calibration.

Instrument Calibration and Verification

The process of calibrating and verifying calibration of turbidimeters at ultra-low turbidity levels is very sensitive to both user technique and the surrounding environment. As measured turbidity levels drop below 1.0 NTU, the interferences caused by bubbles and particulate contamination, which can be slightly problematic at higher levels, can result in a false-positive reading and invalid verification results.

The correlation between turbidity and nephelometric light scatter is a well-defined linear relationship that covers the range of 0.012 to 40.0 NTU. This linearity includes the ultra-low measurement range between 0.012 and 1.00 NTU. Pure water has a turbidity of about 0.012 NTU, which makes measurement of theoretically lower turbidity levels impossible to achieve using aqueous solutions. This linear relationship allows for a single-point calibration to be effective over the entire range of 0.012 to 40.0 NTU. However, it is imperative that the standard be very accurate.

To obtain the most accurate calibration for this linear range, most Hach turbidimeters use a 20.0 NTU formazin standard. This concentration is used because:

1. The standard is easy to prepare accurately from a concentrated stock formazin standard;
2. The standard remains stable long enough to maintain its accuracy for calibration;
3. The standard concentration is in the middle of the linear nephelometric range; and

4. Contamination and bubble errors have less effect on the calibration accuracy at 20 NTU than they would have on a lower calibration standard. Calibrating a turbidimeter using an ultra-low turbidity standard is not necessary, but confirming the accuracy and linearity of the instrument at ultra-low levels is important. The purpose of using ultra-low turbidity verification standards is to confirm the low-end performance of turbidimeters.

StablCal™ Stabilized Formazin Turbidity Standards have been formulated at low turbidity values to provide a means of low-level calibration verification. These standards have been prepared and packaged under strictly controlled conditions in order to provide the highest accuracy possible. In addition, these standards are carefully packaged to minimize contamination from outside sources.

Extraordinary measures are necessary to provide the most accurate means of verifying low-end calibration accuracy of turbidimeters. A single piece of dust or a single particle can cause a spike of more than 0.030 NTU. This can result in errors that exceed 10 percent. The necessary techniques that must be implemented for accurate low-level measurement are described in the next several sections.

Stray Light

Stray light is a significant source of error in low level turbidimetric measurements. Stray light reaches the detectors of an optical system, but does not come from the sample. An instrument responds to both light scattered from the sample and stray light sources within the instrument.

Stray light has a number of sources: sample cells with scratched or imperfect surfaces, reflections within the sample cell compartment, reflections within the optical system, lamps that emit diverging light, and, to a small extent, electronics. In designing an instrument, lenses, apertures, black mirrors, and various light traps are used to help minimize stray light. However, there is a significant contributor to stray light that design cannot fully address: dust contamination within the sample cell compartment and optical compartments of the instrument. Over time, stray light in a turbidimeter will increase as the dust contamination increases and scatters light. In general, process turbidimeters will have lower stray light than laboratory turbidimeters if they are designed without a sample cell compartment.

Unlike the case in spectrophotometry, stray light effects in turbidimetric measurement cannot be “zeroed out”. Some manufacturers attempt to do this with procedures where the user places a sample of “turbidity-free” water in the sample cell compartment and then zeroes the turbidimeter by adjusting the output of the instrument. In doing this, several important aspects of turbidity measurement are overlooked. First, water will always have particles, even when filtered with the best filtration

systems available. In addition, water molecules themselves scatter light. Molecular scattering and the presence of even ultra-small particles contribute to the turbidity of every aqueous sample. When a round 1-inch sample cell containing ultra-low turbidity water is measured, the lowest actual value is approximately 0.010 to 0.015 NTU, depending on the optical system used. The sample cell itself can also play a complicated role in stray light by contributing stray light through any scratches or imperfections that affect the incident beam. The sample cell can also help to focus the beam, which in turn may actually reduce stray light. Another important factor is the set of variables that are introduced when more than one sample cell is used. A second sample cell will contribute stray light effects that can (and probably do) differ significantly from the sample cell used to zero the instrument. All of these considerations are ignored when an instrument is zeroed. A substantial portion of the sample measurement being zeroed out will be falsely attributed to the turbidity of pure water, when in fact there are many factors involved. In this case, over-correction will result and readings will be falsely low.

A quantified value for stray light within a turbidimeter is difficult to determine. One method used to determine the stray light of an instrument is to prepare a formazin suspension of known low-turbidity concentration. This standard is then accurately spiked several times, with the value being measured between each spike. Through the method of standard additions, the theoretical value of the starting standard is calculated and evaluated against the measured value. Subtracting the measured value of the standard from the theoretical value results in a difference that is a close estimate of the stray light. This method of stray light determination is very difficult and requires meticulous cleanliness and very accurate measurement. However, it is an effective method of determining stray light. If low measurements are of importance, stray light must be considered as part of the measurement. By using this method, the estimated instrument stray light may be factored out of the measurement. *Table 1* gives the estimated stray light of Hach turbidimeters.

There are several methods to reduce stray light. First is to use ultra-clean techniques in handling both sample cells and the instrument. The instrument should be kept in a clean, dust-free environment in order to reduce contamination. The instrument should be carefully cleaned at regular intervals. Sample cells should be scrupulously cleaned both inside and out. When not in use, sample cells should be capped to prevent dust contamination. In addition, silicone oil should be coated over the outside of the sample cell in order to fill in minor scratches which will also cause stray light.

Instrument	Range	Stray Light
2100A	0 to 10 NTU	<0.04 NTU
2100 A	0 to 100, 0 to 1000 NTU	<0.5 NTU
SS6/SS6SE	0 to 10000 NTU	<0.04 NTU*
Ratio™, Ratio™ XR	0 to 200, 0 to 2000 NTU	<0.012 NTU
1720C	0 to 100 NTU	<0.01 NTU*
1720D	0 to 100 NTU	<0.008 NTU*
2100P	0 to 1000 NTU	<0.02 NTU
2100N/AN	0 to 10000 NTU	<0.01 NTU
2100 AN IS	0 to 10000 NTU	<0.005 NTU
2100 N IS	0 to 10000 NTU/FNU	<0.5 NTU
Pocket Turbidimeter™	0 to 400 NTU	<0.1 NTU

Table 1. Stray Light of Hach Turbidimeters. Over the years, Hach has continuously lowered the amount of stray light in its turbidimeters.

*Values are not published directly. The SS6 specification is derived from its accuracy specification; the 1720C and 1720D are closely estimated using ultra-low standard spike recovery.

Ultra-Low Measurements

Ultra-low turbidity measurement is the primary interest in turbidity science. This generally applies to the measurement of clean aqueous samples that are less than 1 NTU in turbidity. In these samples, neither individual particles nor any haze will be visible to the naked eye. Examples include drinking water and ultra-pure water applications such as those in the semiconductor or power plant industries.

In the measurement of ultra-low turbidity samples, there are two major sources of error: stray light (discussed above) and particle contamination of the sample. Particle contamination is a significant source of error. Several points address the minimization of this error source and are discussed below:

1. Sample cells and caps must be meticulously cleaned.

The following procedure is recommended for cleaning sample cells.

- a) Wash the sample cells with soap and deionized water.
- b) Immediately follow by soaking the sample cells in a 1:1 Hydrochloric Acid solution for a minimum of one hour. Sample cells can be also be placed in a sonic bath to facilitate removal of particles from the glass surfaces.
- c) Immediately follow by rinsing the sample cells with ultra-filtered deionized water (reverse osmosis filtered or filtered through a 0.2 micron filter). Rinse a minimum of 15 times.
- d) Immediately after rinsing the sample cells, cap the cells to prevent contamination from the air, and to prevent the inner cell walls from drying out.

A simple test can be performed to assess the cleanliness of sample cells. Fill the cleaned sample cell with ultra-filtered deionized water. Allow to stand undisturbed for several minutes. Polish the cell with silicone oil and measure the turbidity. Next, place the same cell in a sonic bath for 5 seconds. Repolish the cell and re-measure the turbidity. DO NOT invert cell during the test. If there is no change in turbidity, then the sample cells can be considered to be clean. If the turbidity increases, the cells are still dirty. The turbidity increase is due to the sonicating of particles from the inner walls of the sample cells, thus contaminating the sample. Another indication of dirty cells is noise in reading. Ultra-clean cells filled with ultra-filtered water will display a very consistent, low turbidity level of less than 0.03 NTU.

2. Sample cells must be indexed.

Once the sample cells have been cleaned, fill them with ultra-filtered, low turbidity water. Let samples stand to allow bubbles to rise. Next, polish the sample cells with silicone oil and measure the turbidity at several points of rotation on the sample cell. Find the orientation where the turbidity reading is the lowest and index this orientation. Use this orientation to perform all sample measurements.

3. Removal of bubbles.

Micro-bubbles can be a source of positive interference in turbidity measurement. The best way to decrease this interference is to let the sample stand for several minutes to allow bubbles to vacate. If the sample needs to be mixed, gently and slowly invert it several times. This will mix the sample without introducing air bubbles that could show up in the measurement.

The application of a vacuum to the sample is also effective. However, care must be taken not to contaminate the sample cell with the vacuum aspiration device. Sonic baths can also be used to eliminate bubbles, but sample cells must be demonstrated to be cleaned using a sonic bath before the bath is further used to remove bubbles. Also, the sonic bath can cause particles in the sample to fracture and change size, or to break away from the sample cell walls back into the sample, thus increasing sample turbidity.

4. Sample cells should be kept polished.

Polishing the outside of sample cells with silicone oil helps prevent particles from attaching to the outer walls. The silicone oil will also aid in reducing stray light by filling in small imperfections that would otherwise scatter light.

5. If possible, use one sample cell.

One sample cell that has been demonstrated to be clean and of high optical quality should be used to measure all samples. When inserted at the same index, the relative turbidity of samples can be accurately compared, eliminating any interference caused by the cell. If more than one cell is needed, they must be indexed. Use the best sample cell to calibrate the lowest point on the turbidimeter. Keep this cell to measure all low turbidity samples.

Instrument Accuracy in the Low Measurement Range

It is very important to verify an instrument's accuracy and response in the range where low level turbidity measurements are taking place. Traditionally accepted turbidity standards are difficult to prepare at these levels and are not stable for any length of time.

Currently, there are two methods available for verifying low-level instrument accuracy. The easiest method involves the use of defined stabilized formazin verification standards. These standards are available in the range of 0.10 to 1.00 NTU and are prepared under stringent synthesis and packaging conditions to achieve the highest accuracy possible. Further, detailed instructions explain the exact use of these standards to achieve an accurate measurement of low-level instrument performance and measurement technique. A second method for assessing instrument performance at ultra-low turbidity levels is to space a measured sample with a known volume of stable standard. To accurately perform this test, the following is needed:

- Ultra-low turbidity water, preferably reverse-osmosis filtered through a 0.2 micron (or smaller) membrane
- Ultra-cleaned glassware, including one sample cell of high optical quality
- A freshly prepared formazin turbidity standard, 20.0 NTU
- A TenSette® Pipet® or other accurate measuring auto-pipette.

With these materials, the user can determine the instrument response to a turbidity spike. Below is an example of how to perform this test:

1. Pipette 25.0 mL of reverse-osmosis filtered water into a ultra-clean turbidimeter sample cell. The sample cell should be dry. Immediately cap this cell.
2. Polish the sample cell and carefully place the cell at index into the turbidimeter.
3. Wait for the reading to stabilize. Normally a 1 to 5 minute wait is necessary to allow for any bubbles to evacuate the sample.
4. Record the stable turbidity reading.
5. Using the 0 to 1.0 mL TenSette® Pipet and a clean pipet tip, spike 0.5 mL of the 20 NTU formazin standard. The formazin standard should be well mixed before use. The amount of turbidity added is 0.39 NTU.
6. Cap the sample cell, and slowly and carefully invert 10 times to mix.
7. Re-polish the sample cell. Place the sample cell at same index into the turbidimeter.
8. Again, wait for 1 to 5 minutes for the reading to stabilize.
9. Record the stable displayed reading.

The difference between the value recorded in step 9 and the value of reverse osmosis water before spiking in step 4 is due to the instrument response to the spike of the 20 NTU formazin added to the sample. Theoretically, this response in turbidity is (in this example) 0.39 NTU. The difference between the instrument response and theoretical values can be estimated as the turbidimeter's error (in NTU) in reading at this level. Stray light from both the instrument and the sample cell are a large portion of this error. This error value can then be subtracted from the low turbidity measurements. This procedure works very well as long as (1) the glassware used is meticulously cleaned; (2) the spiked sample is read immediately after preparation (within 30 minutes); (3) the spike is made accurately; (4) only one sample cell that is indexed the same each time is used; (5) the instrument optics are clean and the instrument is located in a clean environment; and (6) the same sample cell used in this test is used to measure samples.

Characteristics of Ultrapure Water

When water has reached an ultra-clean state, it has several characteristics that can be recognized in performing a turbidity measurement. In order to accurately assess the quality of samples at these levels, all of the discussed techniques must be applied to the preparation and measurement of these samples. The characteristics of ultrapure samples are listed below:

1. The turbidity reading is typically between 0.010 and 0.030 NTU when measured on a properly calibrated laboratory turbidimeter with low stray light.
2. The turbidity reading will be stable (the displayed reading will not vary) out to 0.001 NTU. If the reading fluctuates more than 0.003 NTU, the source is either due to particles or to bubbles moving through the light beam. If the fluctuation in reading is due to bubbles, the bubbles will leave the sample over time and the readings will eventually become stable.
3. The turbidity reading will be unchanged even when the sample undergoes a temperature change.
4. The sample may be colored, but will be highly transparent. No particles will be visible to the naked eye.

Due to their high purity, ultra-clean samples are highly aggressive. Over time such samples can dissolve glass from a sample cell back into a sample to the point where the turbidity will increase. However, this takes time to occur, generally longer than 24 hours. Thus, fresh samples should always be used when making a turbidity measurement.

Ultra-High Turbidity Measurement

Ultra-high turbidity measurements are generally turbidity measurements where nephelometric light scatter can no longer be used to assess particle concentration in samples. In a sample with a measurement path length of 1-inch, nephelometric light-scatter signals begin to decrease at turbidities exceeding 2000 NTU. At this point, an increase in turbidity will result in a decrease in nephelometric signal.

However, other measurements can be used to determine the turbidity of such samples. Three of these are transmitted, forward scatter, and back-scatter methods. Transmitted and forward-scatter signals are inversely proportional to increased turbidity and give good response to 4000 NTU. Above 4000 NTU (when using the standard 1-inch path), transmitted and forward-scatter signals are so low that instrument noise becomes a major interfering factor. On the other hand, back-scatter signals will increase proportionally with increases in turbidity. Back-scatter measurements have been determined to be highly effective at determining turbidity specifically in the range of 1000 to 10000 NTU (and higher). Below 1000 NTU, back-scatter signal levels are very low, and instrument noise begins to interfere with the measurements. With a combination of detectors, turbidity can now be measured from ultra-low to very high levels. See Section IV for how these detectors work together.

The use of ultra-high turbidity measurement has many applications. It is used in the monitoring of fat content in milk, paint resin constituents such as titanium dioxide, liquor solutions in pulp and paper processing mills, and ore slurries in milling operations.

When making ultra-high turbidity measurements, sample cell quality has a large effect on measurement accuracy. Sample cells are not perfectly round, nor is the cell wall of a consistent thickness. These two factors have a dramatic effect on the back-scatter measurement in particular. To minimize the effects of sample cell aberrations, an ultra-high turbidity sample should be read at several points of rotation on a single sample cell. Suggested rotation points are at 0, 90, 180, and 270 degrees from index. These four measurements must be made using the same sample preparation methodology. Measurements should be made during a timed interval after mixing in order to maximize reproducibility in measurement. All the measurements should be averaged and this value used as the turbidity of the sample.

Ultra-high turbidity measurements are generally used as a mechanism for monitoring process control. The user must first determine the relationship of turbidity to varying conditions in the process stream. In determining this relationship, dilutions of the sample are made and the turbidity of each dilution is measured. A plot of turbidity (y-axis) versus each corresponding dilution (x-axis) is then made. The slope of the best fit line will indicate the nature of this relationship. If the slope is

very large (greater than 1), then the response is good and potential interference is minimal in the measurement. If the slope is small (less than 0.1), then interferences are present and are impacting the measurements. In this case, the sample may need to be diluted until the slope increases. Last, if the slope is near zero or is negative, then either the turbidity is still too high and/or the interferences are too large for the measurements to be accurately used. Again, the sample needs to be diluted.

Color can be a major interference in ultra-high turbidity measurements. A possible solution to color interference is to dilute the sample significantly. An alternative to diluting the sample is to determine the wavelength(s) where the sample absorbs light and then perform a turbidity measurement at an alternate wavelength where sample absorbance is minimized. The use of wavelengths in the range of 800 to 860 nm is effective, because most naturally occurring substances do not significantly absorb light in this range.

The ability to make turbidity measurements at ultra-high levels allows simple and accurate physical assessment of a wide array of samples and processes. In general, each process will be unique, and an effort must be made to accurately characterize a sample and its respective processes when using turbidimetric monitoring techniques.

Turbidity vs. Suspended Solids

Traditional solids analyses, usually completed by gravimetric methods, are time-consuming and technique-sensitive. Generally, it takes from two to four hours to complete such an analysis. Thus, if a problem is found, it is often too late to make an easy correction to the process. This leads to costly down time and repairs to fix the problem. However, the turbidity of these samples may be used as a surrogate to the lengthy gravimetric analysis. A correlation needs to be established between the turbidity and total suspended solids (TSS) of the sample. If such a correlation exists, then a turbidimeter can be used to monitor TSS changes in a sample, resulting in a prompt analysis. The response time to a change in the TSS of a process can be reduced from hours to seconds with the use of a turbidimeter.

A procedure has been developed to determine the correlation between turbidity and TSS of a sample. In determining this correlation for a sample, several considerations must be made throughout the entire procedure. These criteria are listed below:

- The sample must not contain solids that are buoyant.
- The sample must be fluid to the extent that it will become homogeneous with mixing and it can be accurately diluted.
- The sample must contain solids that are representative of future samples to be tested.
- The sample constituents must be well known.

- The procedure for determining the correlation must be over in as short a time period as possible.
- The sample must be well mixed for every dilution or measurement that is taken.

- The preparation and measurement methodology of each dilution must be the same throughout the correlation and monitoring of the samples or process.

- The sample temperature must be the same as that in the process of interest. Further, the temperature of all the dilutions must also be the same when performing either turbidity measurements or in the filtration of these samples for gravimetric analysis.

The procedure has been broken down into four steps, which are summarized below:

1. Sample dilution.

Several dilutions of the sample must be prepared to cover the possible range of TSS for the given sample. These dilutions are to be made with turbidity-free water. The sample must be well mixed when making dilutions. Non-aqueous solutions must use a colorless, particle-free solute that matches the chemical and physical characteristics of the sample.

2. Determining the Total Suspended Solids (TSS) of each sample dilution.

The gravimetric determination of each of the dilutions of the sample must be determined. Care must be taken to use consistent methodology throughout the entire set of samples.

3. Measuring the turbidity of each dilution.

All samples must have the turbidity determined. The same methodology of sample preparation and measurement must be consistent for all turbidity readings. For example: each sample is inverted the same number of times, the wait between mixing and recording readings is consistent throughout the procedures, etc.

4. The correlation between the turbidity measurements and the gravimetric measurements of the dilutions is determined.

A graph should be prepared in which total suspended solids in mg/L are displayed on the x-axis and respective turbidity is displayed on the y-axis. A least squares relationship can then be determined. Least squares is a statistical method to verify the relationship and determine the actual turbidity of a sample to within a certain degree of accuracy. A correlation coefficient of 0.9 or greater indicates a workable relationship of turbidity to TSS. By graphically plotting this relationship, one can determine the sensitivity of the correlation in order to gain confidence in the correlation. The greater the slope of this correlation, the greater the sensitivity of turbidity to TSS and the better the correlation will work on the sample.

A copy of this procedure, Method 8366, may be obtained from Hach Company.

IV. Advanced Measurement Techniques: Ratio™ Instrument Design

Introduction

This section is devoted to the design and performance of a relatively new family of Hach turbidimeters that are designed to meet EPA criteria—the 2100N, 2100AN, 2100AN IS, 2100N IS, and the 2100P. All feature ratio methodology and are designed for water and industrial applications.

Why is Ratio™ turbidimeter methodology important? Because of the influence of sample color, the application of strict nephelometric turbidity has been limited, particularly in industrial processes that involve beverages, food products, cell cultures, and dispersed oil in water. Conventional turbidimeters could not separate the effects of color from turbidity measurement. So, in response to the changing needs of the water industry and the demands of “colored liquid” applications, Hach developed a series of instruments that use ratio turbidimeter methodology. These instruments not only eliminate the influence of sample color, but feature significant improvements in performance, convenience, and reliability over their predecessors.

Design Objectives

Five objectives were adopted early in the development of a ratio turbidimeter in order to achieve the highest performance and satisfy the broadest range of applications.

1. The instrument would meet either USEPA or ISO 7027 requirements for water testing.

The first objective ensured that the turbidimeter would meet the needs of the municipal water industry. Although the instrument’s unique features would result in many new applications, water testing was expected to continue as the largest single application for nephelometry. This objective dictated that certain design parameters be followed:

- A tungsten lamp light source would be operated at a filament color temperature between 2200 and 3000 °K for USEPA and be 860 nm with a bandwidth of 60 nm for ISO 7027.
- The light path length within the sample was not to exceed 10 cm.
- Scattered light was detected at $90^\circ \pm 2.5^\circ$. This would serve as the primary detector for the instrument.
- For USEPA compliance, the detector and filter system response would peak between 400 and 600 nm.

2. The instrument would be so stable over the long term that the use of standards would not be routinely required.

The requirement for long-term stability resulted in greater convenience and accuracy. Early nephelometers had front panel standardization controls which had to be set with a standard at each use of the instrument. The ratio turbidimeters achieved such stability that a monthly or quarterly calibration was sufficient. Calibrations were algorithm based, and were easier to perform than previous calibrations. Fewer calibrations meant greater reliance could be placed on primary formazin standards, rather than using secondary standards for calibrations.

3. The instrument would be accurate to approximately plus or minus 0.01 NTU, with stray light less than or equal to 0.010 NTU.

As turbidimeters began to be used with increasing frequency at the lowest end of their ranges, accuracy at very low turbidities became essential. The largest source of error at low turbidities was stray light—that is, light that reaches the detector due to sources other than sample turbidity. Stray light introduced a positive error, which made the sample read more turbid than it actually was. If the stray light of an instrument could be measured, the electronics could be adjusted to compensate. But because experimental determination of stray light was difficult, the preferred solution was to design an optical system with negligible stray light (refer to Section III). This was the course taken in the design of the 2100N, 2100AN, 2100AN IS, 2100N IS, and 2100P turbidimeters.

4. The instrument would have a digital readout directly in NTU units.

Advantages of digital displays for analytical instrumentation are ease of use, freedom from reading errors, increased resolution, and accuracy. Digital displays also give the user information on sample noise and on the quality of low turbidity readings. While analog instruments could be calibrated with nonlinear meter scales, the electronic signal supplied to the digital display would need to be linear if the instrument were to read directly in turbidity units. This requirement had significant impact on the design of the ratio turbidimeters.

5. The instrument would be capable of accurate turbidity measurements, even in highly colored samples.

A number of turbidity problems with colored samples could not be handled by a conventional nephelometer. Color provided a negative interference, attenuating both incident and scattered light, and the turbidity read a lower than it should. The effect was so great for even moderately colored samples that conventional nephelometers could not be used in these applications. Development of the ratio turbidimeter’s high degree of color rejection opened up many new applications for nephelometry.

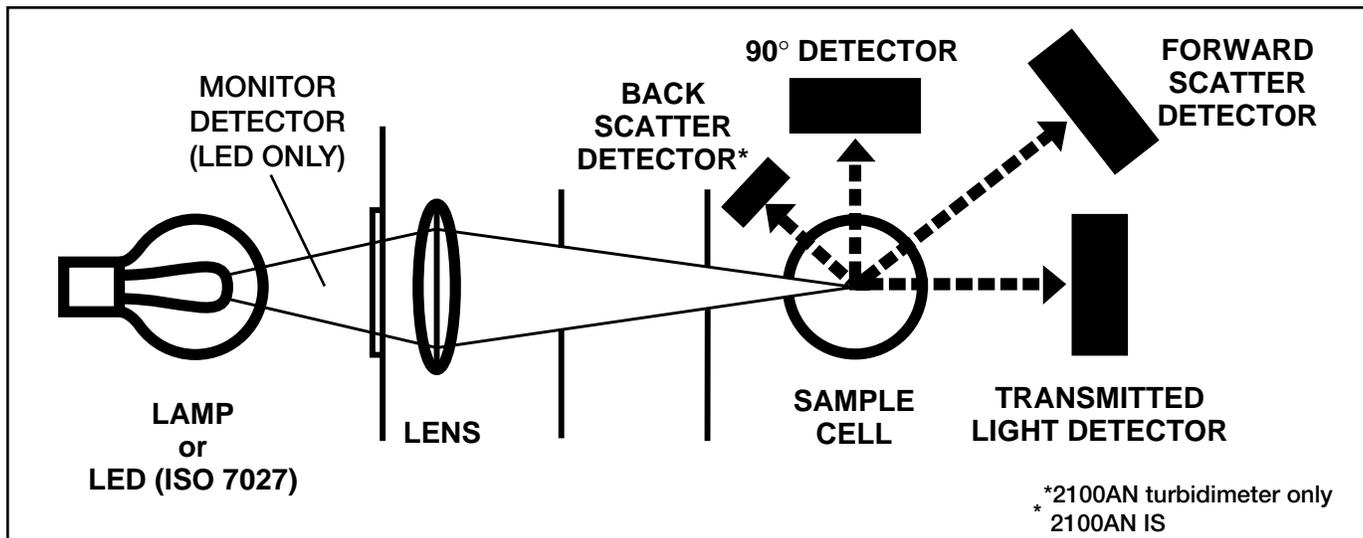


Figure 11. Optical design of Hach ratio turbidimeters.

Optical Design

The ratio turbidimeter's optical configuration is the key to several performance characteristics. Among them are good stability, linearity, sensitivity, low stray light and color rejection. *Figure 11* shows the optical design used in the 2100N, 2100AN 2100 AN IS, or 2100N IS Laboratory Turbidimeters (the 2100N does not have a backscatter detector). The 2100P has a 90° detector and a light detector. The 2100N IS has only a 90° detector.

The 2100N and 2100AN Laboratory Turbidimeters operate on the principle that the amount of light scattered from a sample is proportional to the quantity of particulate material in that sample. Light from a tungsten halogen lamp, operating at a nominal color temperature of 2700 °K, is collected by a set of three polycarbonate lenses. The polycarbonate is able to withstand the temperature extremes from the lamp. The lenses are designed to gather as much light as possible and image the filament of the lamp to the sample cell. A blue infrared (IR) filter in the optical path causes the detector response to peak at a wavelength between 400 and 600 nanometers, in compliance with EPA guidelines. For the 2100AN, an optional interference filter may be used in place of the IR filter so that turbidity measurements can be made with "quasi" monochromatic light. A series of baffles in the path between the lenses and the sample cell catch light scattered from the lens surface to help prevent any stray light from getting to the detectors. All but the final baffle closest to the sample cell are sized so that the caustic that surrounds the light from the lenses barely touches the baffle edges. Also, the final baffle is oversized so that any misalignment of the beam does not cause the edges to glow and increase the instrument's stray light.

Silicon photodiodes in the sample area detect changes in light scattered or transmitted by the sample. A large transmitted-light detector measures the light that passes through the sample. A neutral density filter attenuates the light incident on this detector and the combination is canted at 45 degrees to the incident light, so that reflections from the surface of the filter and detector do not enter the sample cell area. A forward-scatter detector measures the light scattered at 30 degrees from the transmitted direction. A detector at 90 degrees nominal to the forward direction measures light scattered from the sample normal to the incident beam. This detector is mounted out of the plane formed by the light beam and the other detectors. The angle and baffling for this out-of-plane mounting blocks light scattered directly from the sides of the sample cell while collecting light scattered from the light beam. The signals from each of these detectors are then mathematically combined to calculate the turbidity of a sample. The 2100AN contains a fourth, back-scatter detector that measures the light scattered at 138 degrees nominal from the transmitted direction. This detector "sees" light scattered by very turbid samples when the other detectors no longer produce a linear signal. It also extends the measurement range of the turbidimeter up to 10,000 NTU. *Figure 12* (next page) shows the relationship of light scatter to turbidity at the various detectors used in the Hach laboratory turbidimeters.

Lamps and detectors are often the largest source of noise and drift in conventional nephelometers and other optical instruments. Use of advanced detectors removes part of this problem and the use of a ratio system compensates for lamp effects. The turbidity value is derived by ratioing the nephelometric signal against a weighted sum of the transmitted and forward-scattered signals. (At low or moderate turbidity levels, the forward-scattered signal is

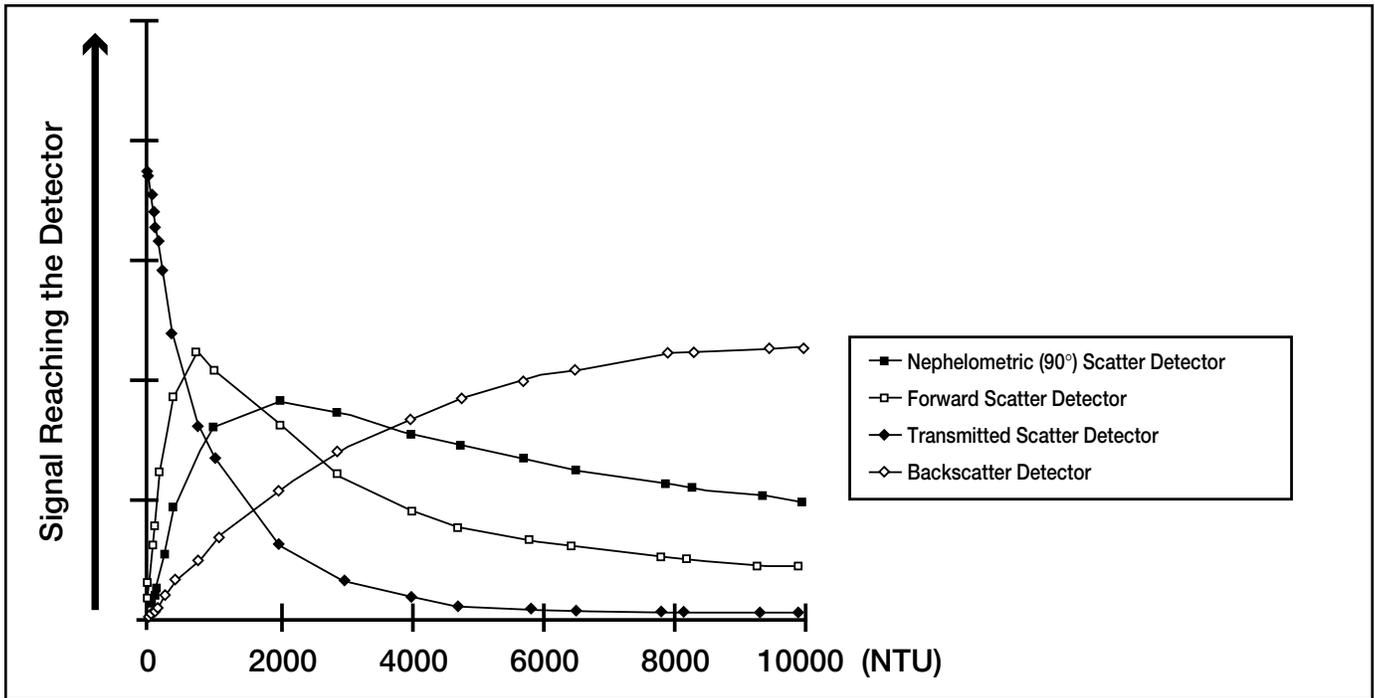


Figure 12. The Relationship of Light Scatter to Turbidity

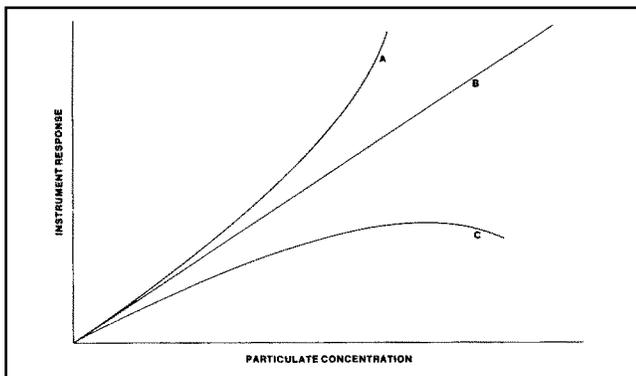


Figure 13. Instrument response vs. particulate concentrations for different optical geometries.

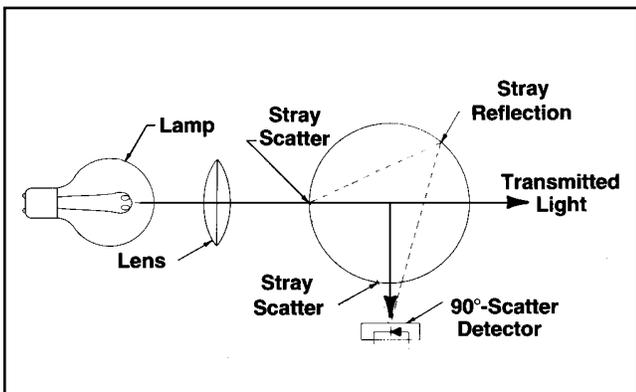


Figure 14. Stray light sources in a turbidimeter.

negligible in comparison to the transmitted signal; the output is just the ratio of 90° scattered light to transmitted light.) This ratioing, which gives the instruments their name, is a key feature in the instrument's excellent long-term stability. In addition to lamp fluctuations, the ratio principle compensates for haze and dust on optics as well as temperature coefficients of detectors and amplifiers. These detectors, operated in a ratio configuration, give the instruments a degree of stability which makes continual standardization unnecessary.

A general characteristic of single-beam nephelometers is to become nonlinear and eventually "go blind" at high turbidity levels, because the increase in light attenuation eventually has a larger effect than the increase in scattering. This behavior is exemplified in *Figure 13* by the curve labeled "C". One might expect that a simple ratio of scattered to transmitted light would extend the range of linearity because the rays traverse at more or less equal distances through the sample and should be affected equally by the attenuation, as is the case for attenuation by color. However, at high turbidity levels, light reaching the detectors is likely to have been scattered more than once. This multiple scattering acts to reduce the distance traversed by the scattered rays, while it can only increase the distance traversed by transmitted rays. *Figure 14* shows a short-cut path along Line 1 that can be taken by a twice-scattered ray. The result is that the transmitted light is more attenuated than the scattered light at high turbidities, causing the instrument response to become nonlinear in the manner of Curve A in *Figure 13*.

2100N, 2100AN and 2100AN IS turbidimeters use the forward-scatter detector to linearize instrument response at high turbidities. The signal from this detector is combined with the transmitted signal in the denominator of the ratio. At lower turbidities, forward scatter is insignificant compared to transmitted light, so that the forward-scatter detector has no effect. At higher turbidities, the increase in forward scatter just compensates for the attenuation of the transmitted beam, and the instrument response is changed from that of Curve A in *Figure 13* to the ideal linear form shown as Curve B. By proper choice of the forward-scatter angle and the magnitude of the correction, the instrument has been made linear over its full range, as required for digital readout directly in NTU.

Low stray-light characteristics are important for accurate measurement of low turbidity samples. The stray light specification of the 2100N, 2100AN, 2100AN IS, 2100N IS and the 2100P turbidimeters (less than 0.01 NTU for the laboratory models and 0.02 NTU for the 2100P) is significantly better than the Hach 2100A Turbidimeter (less than 0.04 NTU). Low stray light is achieved by mounting the 90° detector above the horizontal plane with suitable baffles as shown in *Figure 15*. The figure shows a cross section through the center of the sample cell looking along the axis of the light beam. Notice that the detector still detects light scattered at 90° from the incident beam. Baffles are arranged so that the detector views the volume of sample traversed by the incident beam, but cannot see the back wall of the sample cell above the optical axis. The reason for this arrangement is shown in *Figure 14*. Stray light generally is caused by scatter and reflections from the walls of the sample cell. Neither reflections alone nor scattering at a single surface cause any appreciable stray light to reach the detector in *Figure 14*, but two possible mechanisms are shown. The first shows a scatter event at the beam entrance which deflects a ray along Line 1 toward the detector where it is scattered again upon exiting and reaches the detector. The second path along Line 2 begins with scatter at the beam entrance followed by a reflection from the rear cell wall. The second mechanism is by far the largest source of stray light with an in-plane detector, because reflections (4%) are so much more intense than the scattering (0.1%) at cell walls. The out-of-plane detector shown in *Figure 15* does not see these reflections and stray light is largely eliminated.

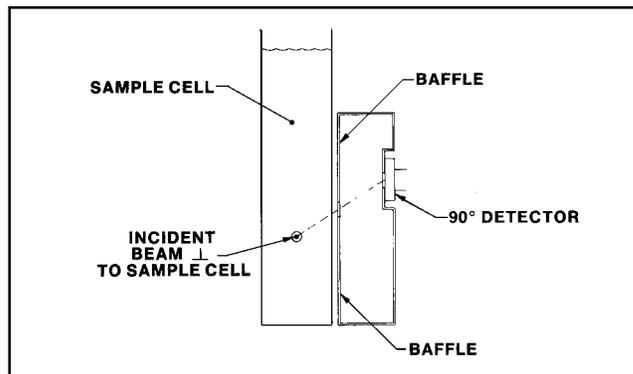


Figure 15. The Ratio™ Turbidimeter's out-of-plane detector minimizes stray light.

Electronic Design

The instrument contains different reading algorithms: ratio turbidity and non-ratio turbidity. (The design algorithm is for the most current turbidimeters). Each is described in the following sections.

Ratio™ Turbidity (Four Point Ratio™ Turbidity*)

The four point ratio calibration algorithm is defined as :

$$T = I_{90} / (d_0 \cdot I_t + d_1 \cdot I_{fs} + d_2 \cdot I_{bs} + d_3 \cdot I_{90})$$

where:

T = Turbidity in NTU Units (0-10,000)

d_0, d_1, d_2, d_3 = Calibration coefficients

I_{90} = Ninety degree detector current

I_t = Transmitted detector current

I_{fs} = Forward scatter detector current

I_{bs} = Back scatter detector current

*U.S. Patent 5,506,679

Non-Ratio™ Turbidity

The non-ratio algorithm is defined as:

$$T = a_0 \cdot I_{90}$$

where:

T = Turbidity in NTU Units (0 - 40)

a_0 = Calibration constant

I_{90} = Ninety degree detector current

Applications

In addition to providing stability, the ratio configuration is the basis for the color rejection of the instrument. Because the transmitted light and the 90°-scatter light traverse nearly equivalent paths through the sample, they are affected equally by color attenuation. Therefore, when the ratio is taken, effects of color are largely reduced. This advantage has opened up many new applications for turbidity measurement, particularly in the food and beverage industries where products often are colored and aesthetic appearance is important.

Figure 16 compares the effect of sample color on a ratio turbidimeter to the same effect on a conventional instrument. In both cases, the instrument was calibrated using formazin suspensions in deionized water. Known amounts of formazin were added to beer (yellow), a rose wine (pink) and a burgundy wine (dark red). Ideally one would obtain the same results in the colored solutions as in water. The conventional instrument's results are very low, as is to be expected in any single-detector nephelometer. The more strongly colored the solution, the more severe the error. At the 100 NTU level, the beer, rose and burgundy read 60, 8 and 4 NTU, respectively, on the conventional nephelometer. The ratio turbidimeter gives much more ideal results—only about 10% low on the average. Notice that color compensation is not quite exact even with the ratio turbidimeter. The residual difference is attributed mainly to differences in the spectral distribution of scattered and transmitted light.

Figure 17 shows the response of a ratio turbidimeter and a conventional turbidimeter to colloidal carbon in water, beer and burgundy. In this case, there is no ideal sensitivity because the turbidity-producing material is not formazin.

There are three major points of interest in these data. First, the ratio turbidimeter is much more sensitive than the conventional turbidimeter to carbon particles. Second, ratio turbidimeter results are nearly independent of color, while the conventional turbidimeter results vary greatly with sample color. Third, the ratio turbidimeter gives results which are linear with carbon concentration.

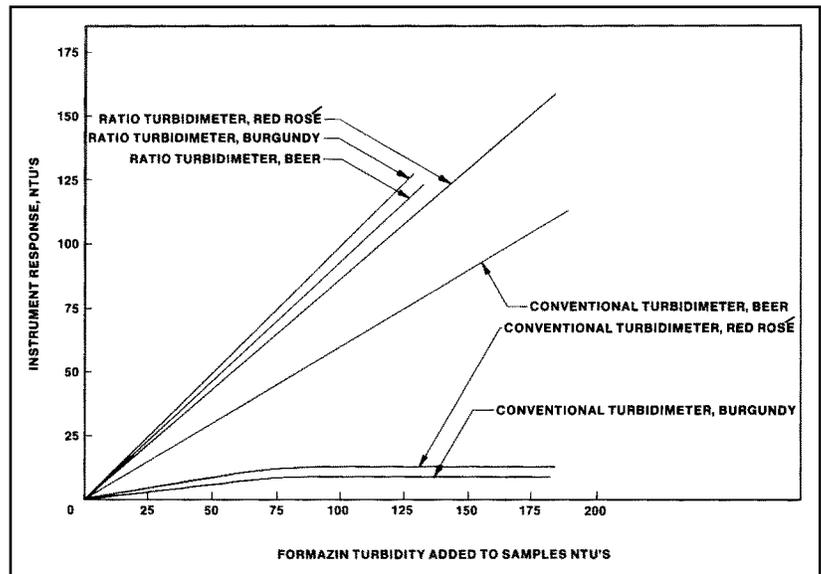


Figure 16. A response comparison of conventional turbidimeter and Ratio™ Turbidimeter to formazin turbidity in wines and beer.

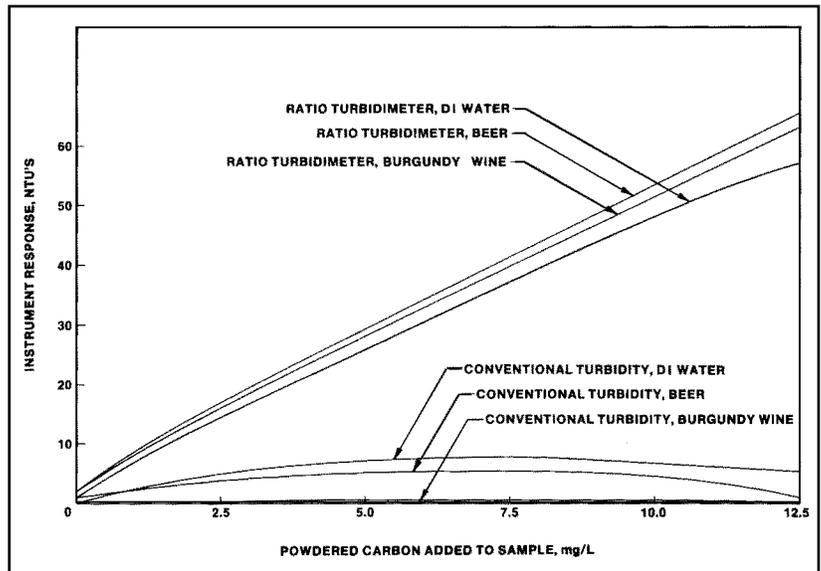


Figure 17. Response comparison of conventional turbidimeter and Ratio™ Turbidimeter to colloidal carbon turbidity in water, wines and beer.

The conventional instrument starts out with a linear response at low concentrations but flattens out and even declines at higher levels. Thus, *Figures 16* and *17* illustrate vastly improved response characteristics when a ratio turbidimeter is compared against a conventional instrument to measure the turbidity of samples characterized by solutions and/or particles that absorb light.

Conclusion

Performance goals established for a ratio turbidimeter design have been achieved. The optical design and ratio system of these turbidimeters have several advantages.

1. In conventional nephelometers, as with other optical instrumentation, lamps and detectors often are the largest source of noise and drift. Use of advanced silicon photodetectors eliminates detector problems. Use of a ratio system compensates for lamp effects such as aging, haze and dust build-up on the optics, and temperature coefficients of detectors and amplifiers. Because the instrument has long-term stability, standardization is not routinely required.
2. The baffle system of the 90° detector provides excellent stray light rejection. This affords greater accuracy in very low turbidity measurements.
3. The forward-scatter detector helps provide a linear response over a wide range without sacrificing sensitivity in lower ranges. The linear response allows the analyst to use a digital readout with the familiar advantages of ease of use, freedom from reading errors, increased resolution, and noise characterization of samples.
4. The ratio system also is the basis for the instrument's color rejection capabilities. Because the transmitted light and the 90°-scatter light traverse nearly equivalent paths through the sample, they are affected equally by the attenuation by color, either dissolved or particulate. When the ratio is taken, the effects of color are thus largely reduced.
5. The back-scatter detector shows a linear response to very high turbidities. This allows turbidity measurement in the 4000 to 10000 NTU range.

Although the 2100N, 2100AN, 2100AN IS, 2100N IS and the 2100P turbidimeters were designed to meet water industry needs, their capabilities will generate many new industrial applications. *Figures 18, 19 and 20* show the 2100AN, 2100N and the 2100P turbidimeters.

Advanced Techniques, Continued: Filters

In turbidity measurement, two distinct methodologies have been developed: *Standard Methods* 2130 and the European ISO 7027 method. Both of these methods were designed and optimized for water samples with low turbidity and minimal color interference. However, there is a huge array of samples where these two methods fail to measure the turbidity accurately with a high degree of sensitivity. These samples generally contain either a strongly colored matrix, colored particles, or both. In



Figure 18. 2100AN Laboratory Turbidimeter



Figure 19. 2100N Laboratory Turbidimeter.



Figure 20. 2100P Portable Turbidimeter.

addition, the sample may fluoresce or have a specific size class of particles. These characteristics will result in major interference that will severely decrease the performance of these two methods. Examples of such samples include: liquid food products, contamination monitoring during the production of various fluids, resins, the effluent of various milling steps, the breakdown of oils, bacterial counts in agars, and in the manufacturing of pulp and paper. This is just a small list of the large array of possibilities.

In the measurement of turbidity by the *Standard Methods* method 2130, the optical characteristics include a very broad spectrum from a tungsten light source. In the 2100AN turbidimeter, this light source can be filtered through the use of various interference filters to produce a specific wavelength of light to be used to perform a turbidity measurement. Through the use of filters, color interference may be completely eliminated and the sensitivity of the instrument to turbidity can be optimized.

When should an alternate filtered light source be considered? Samples that are so strongly colored that the measurement sensitivity of the instrument is severely depressed should be considered ideal candidates for a filtered light source. In addition, samples that fluoresce and cause false high readings should also be measured with an alternate filtered light source. Last, the measurement of colored samples with very small particles that may not be sensitive to either accepted method may be optimized with an alternate light source.

In order to determine spectrally what the interfering color is and how it is affecting the instrument's measurement performance, a spectral scan of the sample is necessary. From this scan, one can determine the wavelengths of light that interfere and then select the appropriate wavelengths of light to optimize the turbidimetric measurement of the sample. If a sample contains very small particles, the shortest wavelength not interfered with by the color within the sample matrix should be selected. If small particles are not of concern, a longer wavelength may be selected. This choice is due to the low sensitivity of long wavelength light to typical sample colors.

When selecting the appropriate filter, one must also be aware of the spectral characteristics of the instrument's light source and detection system. Generally, Hach turbidimeters with a tungsten filament light source have a spectrum that allows for the use of broad band-pass interference filters greater than 600-nm. If a filter is installed that is below 600 nm or has too narrow a band-pass, there will not be enough signal from the light source to allow for an accurate turbidity measurement. Thus, filters greater than 600 nm with a wide band-pass will help to maximize signal output to the detectors of these instruments.

Wavelength	Sample 1	Sample 2	Sample 3
455 nm	37.3	31.4	147
620 nm	0.76	1.13	1.6
860 nm	0.114	0.168	0.627

Table 2. Effect of different light source wavelengths on turbidity readings. 2100AN Turbidimeter. Calibration performed after installing each filter.

An example of an alternate filter system used to optimize turbidity analysis is in the measurement of power transformer insulating oils. These oils are colored and also contain sub-micron sized particles. To maximize the instrument sensitivity to the turbidity of this sample, we needed to find the shortest possible wavelength that would not be influenced by the color of the sample. The filter chosen also had to pass enough energy through the system to allow the turbidimeter to function correctly. A spectral scan performed on the sample indicated there would be color interference at any wavelength below 580-nm. Thus, we selected a 620 nm filter with a band-pass of 40 nm. This maximized the instrument's sensitivity to the turbidity caused by small particles in the sample and at the same time eliminated interference due to color. Further, the filter's broad bandwidth allowed enough energy to pass through for instrument detectors to function properly. *Table 2* shows the oil sample's turbidity at selected wavelengths.

When considering the use of an alternate wavelength for performing turbidity measurements, one must understand that these custom methods are sample, and process-specific. If a custom method is to be transferred to a similar sample process, work should be performed to ensure the method is optimized and functioning properly on the sample of interest.

V. Proper Measurement Techniques

Proper measurement techniques are important in minimizing the effects of instrument variables as well as stray light and air bubbles. Regardless of the instrument used, the measurement will be more accurate, precise and repeatable if attention is centered on the following techniques.

1. Maintain sample cells in good condition.

Cells must be meticulously clean and free from significant scratches. Cleaning is best completed by thorough washing with laboratory soap inside and out, followed by multiple rinses with distilled or deionized water, then capping sample cells to prevent contamination from dust particles in the air (refer to Ultra-Low Measurements section). Cells should be treated on the outside with a thin coating of silicone oil to mask minor imperfections and scratches that may contribute to stray light. The silicone oil should be applied uniformly by wiping the cells with a soft, lint-free cloth. Excessive oil applica-

tions must be avoided. Sample cells should be handled only by the top to avoid deposition of dirt and fingerprints within the light path.

2. Match sample cells.

Once the sample cells have been cleaned, fill them with ultra-low turbidity water. Let samples stand to allow bubbles to rise. Next, polish the sample cells with silicone oil and measure the turbidity at several points of rotation of the sample cell (do not invert between rotations). Find the orientation where the turbidity reading is the lowest and index this orientation. Then, whenever this sample cell is used, be sure it is inserted into the sample cell holder at this same index mark. If possible, use one cell that is consistently inserted at the same index.

3. Degas the sample.

Air or other entrained gases should be removed prior to measurement. Degassing is recommended even if no bubbles are visible. Three methods are commonly used for degassing: addition of a surfactant, application of a partial vacuum, or use of an ultrasonic bath. Addition of a surfactant to the water samples lowers the surface tension of the water, thereby releasing entrained gases. A partial vacuum can be created by using a simple syringe or a vacuum pump. (Application of a vacuum pump is only recommended for ultra-low measurements.) Using an ultrasonic bath may be effective in severe conditions or in viscous samples, but is not recommended for ultra-low measurements.

Use of a vacuum pump or an ultrasonic bath should be approached cautiously. Under certain sample conditions, these techniques can actually increase the presence of gas bubbles, especially when the sample contains volatile components. Further, sonication can contaminate the sample or change the particulate size distribution of the sample.

The easiest, most cost-effective alternative to a vacuum pump for water samples is a 50-cc plastic syringe fitted with a small rubber stopper. After the sample cell is filled with the appropriate volume of sample, the stopper is inserted into the top of the cell with the syringe plunger pushed in. As the plunger is withdrawn, pressure within the cell drops and gas bubbles escape. All parts of the syringe should be kept clean and care must be taken not to contaminate the sample.

4. Samples should be measured immediately to prevent temperature and settling from changing the sample's turbidimetric characteristics.

Dilutions should be avoided when possible because a dilution may change the characteristics of particles which may be suspended. Suspended particles causing turbidity in the original sample may dissolve when the sample is diluted. Thus, the measurement would not be representative of the original sample. Similarly, temperature changes may affect solubility of sample components. Samples should be measured at the same temperature as at collection.

If dilutions of aqueous samples are necessary, they should be made with ultra-filtered, turbidity-free water. This is best prepared through use of a reverse osmosis with a filter of 0.2 microns or less.

Variation Among Instruments

Perhaps the most significant practical consideration in turbidimetric measurement is the difference in measured values among different instruments that have been calibrated with the sample standard material. As explained previously, differences in the spectral characteristics of the light source/detector combination are the most important reason for different instruments giving different values for the same sample. At low NTU measurements, stray light is also a large variable. *Table 1*, page 12, shows variations in stray light among different Hach instruments.

The seriousness of this problem and the misunderstanding associated with it concerns both users and manufacturers of nephelometers and turbidimeters. The authors of *Standard Methods* (19th edition) have attempted to minimize variation by specifying critical components of an instrument for turbidimetric measurement:

1. Light source: Tungsten-filament lamp operated at a color temperature between 2,200 and 3,000 °K.
2. Distance traversed by incident light and scattered light within the sample tube: not to exceed 10 centimeters.
3. Angle of light acceptance by detector: centered at 90° to the incident light path and not to exceed $\pm 30^\circ$ from 90°. The detector and filter systems, if used, shall have a spectral peak response between 400 and 600 nm.

The tolerance established by these specifications still allows substantial variability among instruments. Successful correlation of measurements from different turbidity stations can be achieved by using the same instrument model at each station.

VI. Innovative Approaches To Process Turbidity Measurement

A pioneer in turbidimetric measurement, Hach Company has developed portable, laboratory, and process instruments to minimize the practical problems discussed previously and make turbidimetric measurement as error-free and reliable as possible. Laboratory instruments were discussed in detail in earlier sections. This section will focus on process instruments.

Process Turbidimeters

Process turbidimetry presents unique challenges. Operation must be continuous. Control signals must be immediately available to provide process feedback. The instrument itself must have a wide dynamic range and be as maintenance-free as possible. Hach engineers have addressed these design constraints in several ways. Our main concerns were to eliminate the use of a sample cell and to minimize or eliminate contact between the sample and the instrument optical components.

Low-Range Design

Figure 21 is a graphic representation of the Hach 1720D Turbidimeter, designed specifically for improved bubble rejection and highly accurate turbidity readings in the lower ranges. In the 1720D, bubbles are eliminated before entering the primary chamber of the body through a network of baffles that force the sample through chambers exposed to the atmosphere. The greater distance between the baffle network and the measuring chamber in the Model 1720D causes less likelihood of trapped bubbles rising into the measuring chamber and producing reading fluctuations.

The 1720D Turbidimeter is also a “smart sensor.” It features a microprocessor and all supporting electronics and optical components housed in one sensor head. The instrument sends data to other network devices linked through a communications module known as the AquaTrend® Interface Module via a digital fieldbus protocol called LonWorks. This communication link between the smart sensors and the AquaTrend® Interface enables customers to add or remove devices (instruments) and create a network topology specific to their application needs. The AquaTrend® interface can monitor and control up to eight turbidity sensors at one time. This networked system approach provides the capability to install multiple AquaTrend® Interface Modules for remote monitoring from different locations. Customers can place the 1720D sensor up to 400 meters (300 feet) away from the AquaTrend® Interface.

The display functions of the 1720D Turbidimeter are controlled through a separate, menu-based graphical user interface incorporated into the AquaTrend® module. Users can display data from and communicate with up to eight turbidimeters. User-friendly menu screens prompt the user for calibration, alarm and recorded set-up, network configuration, security functions, display set-up, and diagnostic options.

The AquaTrend® module’s user-friendly menus minimize the button-pushing and entry of alphanumeric codes that users experienced with older model turbidimeters. The module is housed in a NEMA 4X/IP66 (indoor) enclosure and features a keypad that is easily accessible.

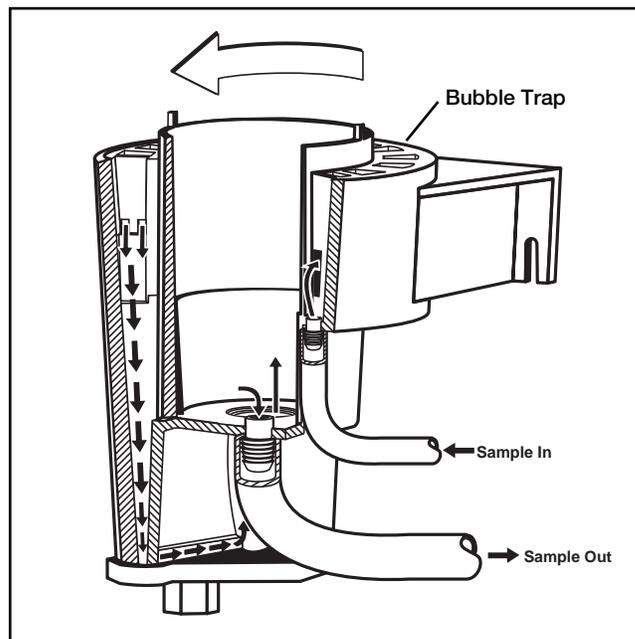


Figure 21. Hach 1720D Process Turbidimeter design.

The 1720D has a 30 percent performance improvement in response when compared to similar instruments. At a flow rate of 500 mL/min, the 1720D’s average response time is 3.5 minutes. This faster response time is a result of lower sample volume (approximately 0.9L). The 1720D’s advanced keyhole design reduces stray light, providing more accurate (2% from 0 - 40 NTU and 5% from 40 - 100 NTU) readings. Combined with the design of the new bubble trap, the instrument significantly reduces entrained air in the sample, resulting in fewer turbidity reading fluctuations.

Wide-Range Design

Figure 22 represents another approach to process turbidimetry. The Surface Scatter® Method of measurement used in Hach Surface Scatter® 6 and Surface Scatter® 6/SE (Severe Environment) turbidimeters is designed for wide-range measurement. This patented design completely eliminates contact between the sample and the instrument’s optical components.

The light source and detector are mounted above the turbidimeter body, isolating optical components from the sample to provide virtually maintenance-free operation. Sample is brought into the center of the body, rising to the top and overflowing a weir into a drain. Flow rate is controlled to allow the overflow to form an optically flat surface.

The light beam is focused on the sample surface at an acute angle. Light striking particles within the illuminated area is scattered, refracted or reflected as shown. Light not scattered is either refracted down the body of the instrument and absorbed, or is reflected off the sample surface and absorbed within the enclosure. Scattered light is detected by the photodetector and the signal from the detector is fed to the control unit.

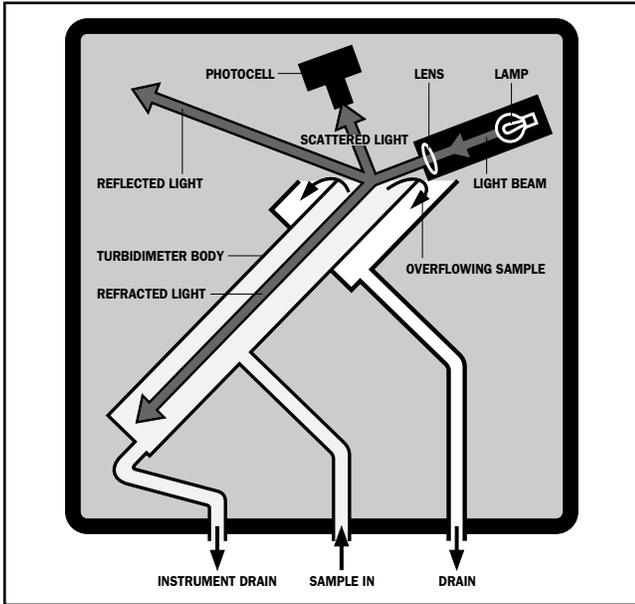


Figure 22. Hach Surface Scatter® 6 Process Turbidimeter design.



Figure 23. Hach Backwash Turbidimeter

As turbidity increases, the amount of sample illuminated by the beam decreases. In effect, this adjusts the light path length to compensate for higher turbidity levels, allowing the instrument to achieve an extremely wide response range of nearly six decades, from 0.01 to 9999 NTU.

To complement the advantages of isolated optics in reducing maintenance requirements, large-diameter plumbing prevents clogging when monitoring high solids samples. The inclined turbidimeter body serves as a trap for settleable solids that could interfere with measurement and the drain at the bottom of the instrument allows periodic purging of accumulated solids.

For very high solids, the bottom drain can be operated in the open position and flow increased to continuously purge solids from the instrument.

Backwash Turbidimeter

Excess backwashing per cycle can waste thousands of gallons of water. Designed specifically to monitor filter bed backwashing, the Backwash Turbidimeter (*Figure 23*) measures transmittance, and is capable of operating over a wide range of turbidity. The sensor is designed to be mounted directly in the wash water trough, providing rapid response to wash water clarity. Measurement is made by focusing the output of a light emitting diode (LED) through the sample as it flows through the center of the sensor assembly. Light transmitted through the sample is measured by a photodetector. Suspended solids will absorb and scatter some of the light, reducing transmittance. At the beginning of the cycle, light transmittance is standardized to read 100% on the clear, filtered water used to wash the filters. Light transmittance drops rapidly as solids trapped by the filter media are released into the wash water. As solids are washed away, wash water effluent clears and transmittance increases. By referencing clear wash water and sensing when filter cleaning is effectively complete, the backwash cycle can be kept to the shortest practical duration, achieving maximum filter washing efficiency.

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