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Turbidity Measurement

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- 62.1 Introduction
- 62.2 Extinction and Turbidity: Particles in a Nonabsorbing Medium
- 62.3 Turbidity Due to Density Fluctuations in Pure Fluids
- 62.4 Design of Laboratory Instruments
Single-Beam Instruments: Optics • Single-Beam Instruments: Electronics • Dual-Beam Instruments: Optics • Dual-Beam Instruments: Electronics
- 62.5 Limitations
References

62.1 Introduction

For nearly 50 years, turbidity measurements have been used to perform a wide variety of physical measurements. These include the determination of particle concentration per unit volume when the scattering cross-section per particle is known, the determination of particle size (scattering cross section) when the concentration of particles is known [1–3], and the determination of some of the critical exponents associated with second-order and nearly second order phase transitions [4–7].

The basic ideas necessary to understand turbidity measurements are fairly simple. In the absence of reflection losses, when a weak beam of light passes through a dielectric sample, the two processes most responsible for reducing the intensity of the transmitted beam are absorption and scattering. The reduction in transmitted light intensity due to scattering is called the sample's turbidity. Extinction includes the effects of both absorption and scattering. The Beer-Lambert or Lambert law describes the effects of both absorption and turbidity on the transmitted intensity. This law is written as

$$I_T = I_0 \exp-(\alpha + \tau)l \quad (62.1)$$

where I_T = intensity of the light transmitted through the sample, I_0 = intensity of the light incident on the sample, α = absorption coefficient per unit length, τ = turbidity per unit length, and l = length of the light path in the sample. As discussed below, it is more correct to use powers rather than intensities, thus this equation should be written as:

$$P_T = P_0 \exp-(\alpha + \tau)l \quad (62.2)$$

The most general situation is to have an absorbing medium with absorbing and scattering particles embedded within it; however, the focus here is on the simpler case of nonabsorbing medium and consider the two most common cases: nonabsorbing particles in medium and scattering caused by fluctuations in the medium itself.

Instruments generally fall into two categories: commercial and laboratory constructed. The commercial units are of two general types: (a) attachments to spectrophotometers, and (b) white-light turbidity meters, which operate under ambient conditions. Anyone interested in the former should consult the catalog of accessories for the instrument in question. Those interested in the latter should check under “nephelometers” in scientific supply catalogs. Units of this type perform their designed function admirably and probably are sufficient for routine work. However, they may need modification for the more specialized measurements performed in many research laboratories. For this reason, it is common to construct special laboratory instruments. These come in at least two types, most commonly either single-beam or dual-beam instruments. The single-beam instrument usually has an intensity-stabilized light source, whereas the dual-beam instrument corrects for drift in the light source and reflection losses by either electronically or mathematically taking the ratio of the transmitted light power and a reference beam power.

The balance of this chapter is divided into three parts. The first part briefly discusses the physical basis of turbidity measurements and demonstrates how such measurements may be used to infer the scattering cross section of the particles in the solution or the concentration of the scatters in the solution. The second section discusses turbidity of pure fluids and shows how certain critical exponents may be determined from such measurements. The last section discusses laboratory instruments and the relative trade-offs involved in such instruments.

62.2 Extinction and Turbidity: Particles in a Nonabsorbing Medium

Suppose that electromagnetic radiation is incident upon a slab of medium consisting of randomly positioned particles and that the transmitted radiation is detected as shown in [Figure 62.1](#). For the present discussion, assume that the source and detector are in the medium. The radiation that is received by the detector will be less than that incident on the slab because of the presence of the particles in the medium—the particles have caused extinction (or attenuation) of the beam. The extinction of the radiation depends on two physical processes, scattering and absorption, whereas the turbidity depends only on scattering. In scattering, there is no change in the total energy of the radiation; rather, some of

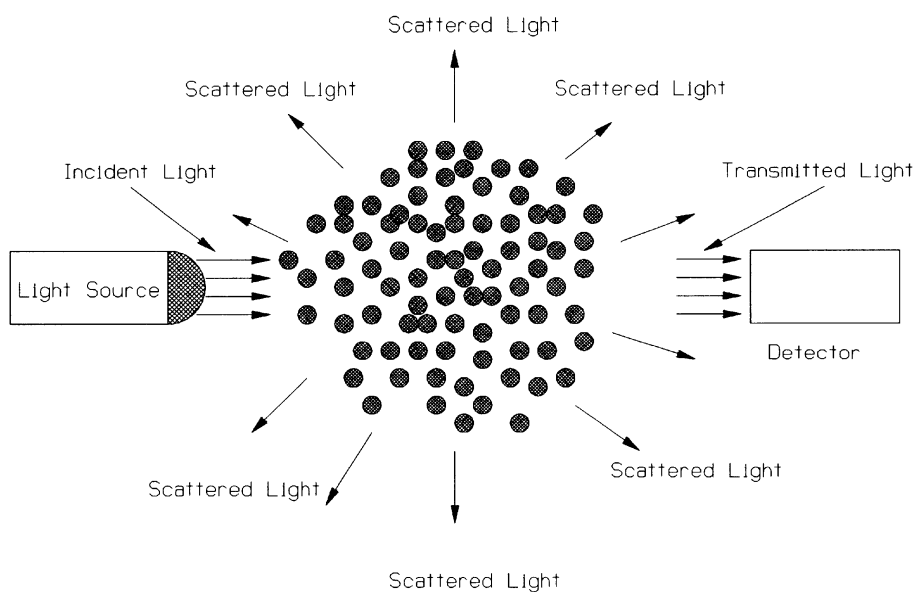


FIGURE 62.1 Idealized experiment indicating the physical basis of turbidity.

the incident radiation is redistributed away from the incident direction. In absorption, some of the energy of the incident beam is transformed into other energy forms. This extinction of the beam is rather complicated; it will, in general, depend on the chemical composition, size, shape, number, and orientation of the particles; the chemical composition of the medium; and the frequency and polarization of the incident radiation [2,3].

In discussions of scattering one often focuses on the *cross sections*, C_i , of the particles. On the basis of conservation of energy one must write:

$$C_{\text{ext}} = C_{\text{scatt}} + C_{\text{abs}} \quad (62.3)$$

where C_{ext} , C_{scatt} , and C_{abs} = cross sections for extinction, scattering, and absorption, respectively. These cross sections all have the dimension of area, and in all cases a larger cross section (area) indicates a larger effect, and a smaller cross section a smaller effect. In general the cross section will depend on all the intensive quantities that describe the extinction. Finally, note that for nonabsorbing media, $C_{\text{abs}} = 0$.

To see how this relates to the measured turbidity, assume now that the medium is nonabsorbing, that all the particles are nonabsorbing and have the same scattering cross section (C), and that there are n of these particles per unit volume. Then, one obtains the following expression for the transmitted light power:

$$P_T = P_0 \exp(-nCl) \quad (62.4)$$

where P_T = transmitted power, and P_0 = incident power. We have switched from intensity to power because power is the quantity detected, and power is independent of the details of the spatial distribution of electromagnetic radiation. Upon noting this change and comparing this to Eq. 62.2, when $\alpha = 0$, it is clear that the turbidity can be expressed as

$$\tau = nC \quad (62.5)$$

Thus, a measured turbidity can be related to C_{scatt} if n is known, or n may be determined if C_{scatt} is known. The difficulty is then in determining C_{scatt} . There are a number of approaches that can be used. For well characterized particles, theoretical expressions may be determined [2]. In the absence of such theory, measurements may be made as a function of concentration and then, since $\tau = nC$, C may be determined. The generalizations to account for nonmonochromatic beams and extinction by a collection of noninteracting particles of the same type but different sizes are straightforward. The simplest generalization to include different sizes assumes that there is one parameter, ζ , that describes the distribution of particle size and the corresponding C_{scatt} [1]. That is, let $C_{\text{scatt}}(\zeta)$ be the scattering cross section for a particle characterized by the parameter (for instance, radius) ζ , and let the number per unit volume with parameter between ζ and $\zeta + d\zeta$ be $N(\zeta)d\zeta$, such that

$$n = \int_0^{\infty} N(\zeta) d\zeta$$

Then

$$\tau = \int_0^{\infty} C_{\text{scatt}}(\zeta) N(\zeta) d\zeta \quad (62.6)$$

A similar integral exists when the incident radiation is not monochromatic, but, in this case, the average is over the wavelength variation of the incident radiation.

62.3 Turbidity Due to Density Fluctuations in Pure Fluids

It is well known that even in very pure and well filtered liquids, in which there are essentially no particles, there is still some reduction in the detected power due to scattering [3]. The explanation is that there are always thermal fluctuations in the dielectric constant of the media, ϵ , and it is these fluctuations from the mean dielectric constant that lead to the scattering of light. Through application of thermodynamic and statistical mechanical principles [3], the following expression for the turbidity results:

$$\tau = \frac{8\pi^3}{2\lambda^4} \left[\rho \left(\frac{\partial \epsilon}{\partial \rho} \right)_T \right]^2 kT \beta_T \quad (62.7)$$

where ρ = density, ϵ = dielectric constant, k = Boltzmann's constant, T = absolute temperature, λ = wavelength of the incident light, and β_T = isothermal compressibility. Near a second order phase transition the fluctuations become correlated over larger distances, and this expression must be generalized to include the effects of this increase in the *correlation length*, ξ . In this case the turbidity is given by [5]

$$\tau = A\pi\beta_T \left[\frac{2\alpha^2 + 2\alpha + 1}{\alpha^3} \ln(1 + 2\alpha) - \frac{2(1 + \alpha)}{\alpha^2} \right] \quad (62.8)$$

where

$$A = \frac{\pi^2}{\lambda^4} \left[\rho \left(\frac{\partial \epsilon}{\partial \rho} \right)_T \right]^2 kT \quad \text{and} \quad \alpha \equiv 2 \left(\frac{2\pi n \xi}{\lambda} \right)^2$$

where n is the (mean) index of refraction of the fluid. Both the isothermal compressibility and the correlation length exhibit approximate power-law behavior of the form

$$\beta_T, \xi \sim \left(\frac{T_c - T}{T_c} \right)^{-x_i} \quad (62.9)$$

near these phase transitions. Thus, a measurement of $\tau(T)$ allows the determination of the critical exponents, x_i , and the values of β_T and ξ far from the phase transition. This technique has been generalized to binary liquid mixtures, liquid crystals, and other systems. In these cases, the isothermal compressibility is replaced by the appropriate generalized susceptibility. There are also, in some cases, small corrections to the above expressions. These can also be found in References 8–10.

62.4 Design of Laboratory Instruments

When more exact measurements are required than can be obtained using commercial instruments, and other enhancements such as mK temperature and/or pressure controlled sample chamber are required, it is common to construct a turbidity instrument. There are basically two types of instruments (single-beam and dual-beam). With both types of instruments, both ac and dc detection schemes are possible. Generally, the long-term time stability of synchronous ac detection techniques is superior to dc techniques. This section discusses all of these techniques.

Single-Beam Instruments: Optics

The basic optical design of a single-beam instrument is shown in [Figure 62.2](#). The light source is a low power (1 to 5 mW) vertically polarized He-Ne laser. It is important to use a polarized laser. The

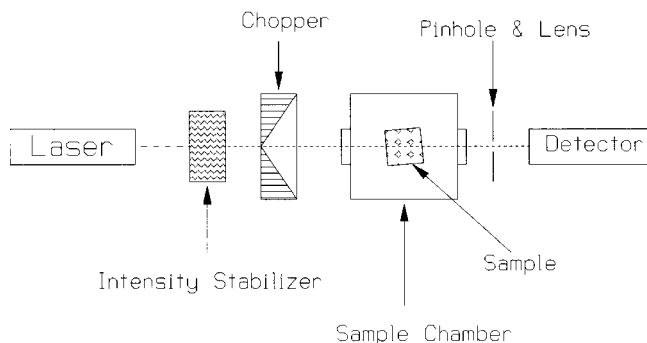


FIGURE 62.2 Block diagram of the optics for a single-beam turbidity apparatus.

polarization direction of an unpolarized laser wanders, and this can lead to time-dependent reflection coefficients from the various surfaces in this instrument, and hence reduced performance. The beam passes through a laser intensity stabilizer. This device reduces long-term drift in the laser power to ≤ 0.1 percent, thus allowing single-beam operation. Table 62.1 shows several commercial intensity stabilizers. To reduce any possible heating of the sample due to absorption, the beam is then passed through a neutral density filter, which attenuates the beam further to a level of 50 to 100 μW . The next item in the beam line depends on the detection scheme. For ac operation a light chopper is inserted into the beam line, while for dc detection nothing else is required before the sample. An output from the chopper is used for synchronous detection. The sample chamber then follows. This chamber requires an input and an output port and a design that precludes interference of any beam with other reflected beams. Other design details are determined by the materials to be studied and any required external factors that are to be controlled. After the beam has been transmitted through the sample, it passes through either a pinhole or a lens-pinhole combination [11, 12]. This results in a small angle of acceptance for the detector which, in turn, reduces the scattered light at small angles from the transmitted beam that reaches the detector. A detector then completes the optical train. For most applications, a *pin* photodiode is an excellent, inexpensive detector; however, in some applications, other types of detectors may be superior.

TABLE 62.1 Commercial Laser Intensity Stabilizers

Manufacturer/Supplier	Model	Approximate Price	Comment
Thor Labs 435 Route 206 P.O. Box 366 Newton, NJ 07860-0366 www.thorlabs.com	CR200	\$1200	Good low-cost, special-purpose unit
Cambridge Research and Instrumentation 21 Erie St. Cambridge, MA 02139 (617) 491-2627	LPC-VIS	\$5000	Outstanding for general use

Single-Beam Systems: Electronics

For both synchronous and dc detection, the output of the photodiode, which is a current device, must be transformed into a voltage using a current-to-voltage converter (CVC). It is important not to use just a resistor for this function. The simplest workable current-to-voltage converter uses an FET-input operation amplifier such as an LM-11 and one resistor. The circuit, also known as a transimpedance amplifier, is standard and can be found in many sources [13].

When dc detection is used, the output voltage from the CVC is read on a voltmeter. The relationship between this voltage and the turbidity will be discussed below. The stability of dc operation is greatly improved by maintaining the photodiode and the electronics at a stable temperature. The drifts in detector

efficiency and in component values associated with temperature changes can limit the accuracy of the instrument. Furthermore, the detector must be shielded from stray light, which means the instrument must be operated in a darkened room or under a light tight cover. Such covers may cause excessive heating of the laser and the system. A “spike” filter that passes the wavelength of the laser may also assist in solving this problem.

When synchronous ac detection is used, the output from the CVC is the input to a lock-in amplifier which is synchronized to the chopper. Commercial units are available and can be used. One can also construct a simple lock-in using an Analog Devices AD-630 balanced modulator/demodulator, a phase shifter to ensure that the reference signal and the transmitted signal are in phase, and an RC filter. The output voltage from the RC filter is then read with a dc voltmeter. The necessary wiring diagrams are available from Analog Devices [14]. Synchronous detection has the advantage of having lower $1/f$ noise than dc circuits. Also, synchronous detection can discriminate against signals not synchronized with the reference, and hence offers much greater immunity to room lights and other stray light sources. The advantages of such detection are discussed elsewhere [13, 15].

Single-beam techniques are most useful for measuring changes in turbidity. To see this, note that the voltage output from the current-to-voltage converter or the lock-in, V_t , is given by $V_t = AP_T$, where A is an instrument constant that includes factors such as current-to-voltage gain, light power level to current conversion in the photodiode, reflection losses from the various interfaces, incident light power, gain of the lock-in, and so on. Now, P_T is given by Equation 62.2, hence V_{dc} , the measured dc voltage may be written as:

$$V_{dc} = B \exp(-(\alpha + \tau)) \quad (62.10)$$

where $B = AP_0$ is another constant, and we have included absorption. B may be determined by putting a solution of known extinction in the instrument and solving Equation 62.10 for B . Then, knowing l , α , B , and V_{dc} , the turbidity may be found by solving Equation 62.10 for τ , that is

$$\tau = \frac{1}{l} \ln\left(\frac{V_{dc}}{B}\right) - \alpha \quad (62.11)$$

This technique is rather limited if a large number of different samples must be compared. For a given sample, the change in turbidity is easily measured as a function of externally controlled parameters. However, putting samples into and taking them out of the instrument usually produces small random errors that slightly change the instrumental constant A and degrade performance. In some cases, the difference in turbidity between two samples may be small and result in a situation in which one must deal with a small difference of large numbers. This situation may be rectified using dual-beam instruments.

Dual-Beam Instruments: Optics

The optical design of a dual-beam, two-detector instrument is shown in [Figure 62.3](#). The first several parts of the optical train are the same as for the single-beam instrument, and the same comments apply in this case. The first real difference is that there need not be an intensity stabilizer in the dual-beam system. However, inclusion of the intensity stabilizer may improve system performance. The second difference is the inclusion of a beam splitter which splits the laser beam into two parts. We have found that a microscope slide works well as a beam splitter [16]. One of these beams (usually the reflected beam) becomes a reference beam that passes through a reference sample. The other passes through the sample as in the single-beam instrument. The beams from these two paths go through lens-pinhole combinations and fall on detectors. All of the comments that apply to the single-beam instrument also apply here. The associated electronics are also identical. Once more, both dc and ac detection may be used. Experience in our laboratory shows that the best results are obtained when the sample signal is

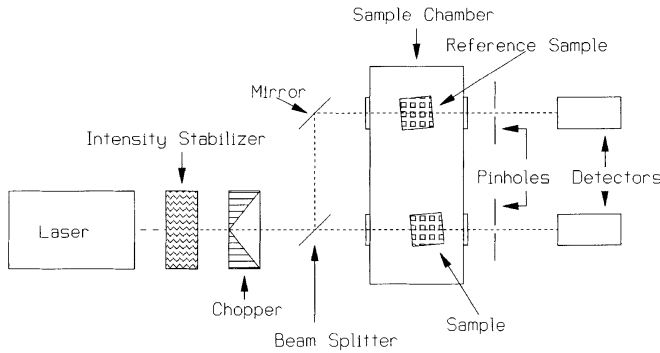


FIGURE 62.3 Block diagram of the optics for a dual-beam, two-detector turbidity apparatus.

simultaneously divided by the reference signal using an integrated circuit divider. A modification that uses two beams and one detector is shown in Figure 62.4. This modified design eliminates the need for absolute stability of two separate detectors but requires somewhat more complex optics.

The following analysis assumes that the measured output is the ratio of the sample signal voltage to the reference signal voltage. Let the voltage output from the detector's CVC be V_{sig} , and the voltage output of the reference signal detector's CVC be V_{ref} . Then

$$V_{\text{sig}} = AP_T \quad (62.12)$$

and

$$V_{\text{ref}} = CP_R \quad (62.13)$$

where A and C = instrumental constants totally analogous to the instrumental constant A above, and P_R = the power of the reference beam at the detector. It is important to realize that A and C are constant, but they need not be identical. The output voltage ratio, V_{out} is given by:

$$V_{\text{out}} = \frac{V_{\text{sig}}}{V_{\text{ref}}} = \frac{AP_T}{CP_R} = D \frac{P_T}{P_R} \quad (62.14)$$

where $D = A/C$ is a constant. Note that, in this arrangement, common multiplicative noise on the two voltages will tend to cancel out. Now P_T can be replaced by Equation 62.1, and P_R is given as

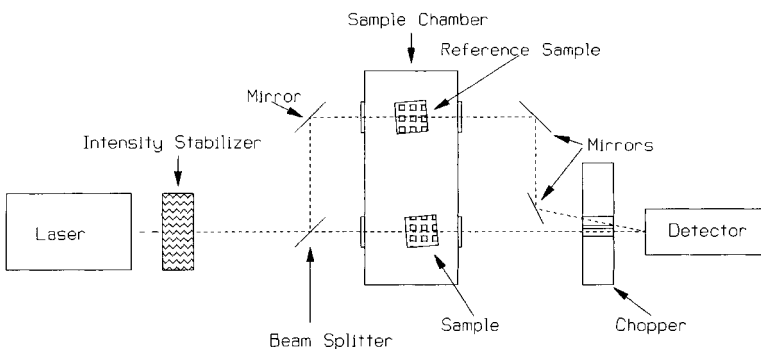


FIGURE 62.4 Block diagram of the optics for a dual-beam, one-detector turbidity apparatus.

$$P_R = f * P_0 \exp -(\alpha_R + \tau_R) l_R \quad (62.15)$$

where α_R = absorption, τ_R = turbidity of the sample in the reference beam, l_R = thickness of the sample in the reference beam, and f is a constant determined by the beam splitter. Then, assuming that l_R is the same as l the following expression results:

$$V_{out} = D \frac{P_0 \exp -(\alpha + \tau) l}{f * P_0 \exp -(\alpha_R + \tau_R) l} \quad (62.16)$$

and thus:

$$\tau = - \frac{1}{l} \ln \left(\frac{V_{out}}{D'} \right) + \tau_R - \alpha + \alpha_R \quad (62.17)$$

where $D' = D/f$. Often, this can be considerably simplified when the reference sample is a pure liquid because then τ_R is of order 10^{-5} , and α_R is totally negligible. Normally, the reference sample is chosen so that its optical properties approach those of the sample in the case where the concentration of particles is low or the system is far from a phase transition. The constant D' may be determined by using the same sample in both the reference and the signal arms of the instrument—in this case $V_{out} = D'$.

Dual-Beam Instruments: Electronics

The electronics for dc detection consists of two CVC converters, one for each detector. The voltage outputs from these may be read directly. However, experiments indicate that greater stability is achieved by simultaneously dividing these two signal outputs as discussed above. In our laboratory, this is accomplished using an Analog Devices AD-532 internally trimmed integrated circuit divider. These can be purchased with different accuracies. In the present application, they typically perform slightly better than the factory specifications indicate. The circuit details are available from Analog Devices [17].

The electronics for ac detection generally consist of two synchronous detectors followed by division of the sample signal by the reference signal. Once more, this may be accomplished using two Analog Devices AD-630 balanced modulator/demodulators or two commercial lock-in amplifiers. Division can be accomplished in the same way as in the dc technique section.

62.5 Limitations

Highly turbid samples, which transmit very little light, may be difficult to measure using a photodiode. In such cases, the photodiode in the sample arm may be replaced with a photomultiplier (PM). In this case, a chopper can be used to reduce the effects of the dark signal from the PM. The outputs, when the signal is present and when it is blocked, are both measured and averaged (preferably digitally), and the difference is computed. By counting for a fixed number of reference counts (requiring another PM), drift in the source may be eliminated. A Stanford Research Instruments photon counter [18] may be configured in this mode. Furthermore, unless extreme precautions are taken in this situation, erroneous results may occur because the scattered power is as large or larger the transmitted beam power.

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