

(25)

15

Nephelometry and Turbidimetry

15.1 Introductory

Nephelometry and turbidimetry are techniques of analysis that are closely allied to colorimetry. Much of the theory and equipment used in colorimetry apply with little modification to both these techniques.

Both nephelometry and turbidimetry are based on the scattering of light by non-transparent particles suspended in a solution. However, the two techniques differ only in the manner of measuring the scattered radiation.

When light is allowed to pass through a suspension, the part of the incident radiant energy is dissipated by absorption, reflection, and refraction while the remainder is transmitted. Measurement of the intensity of the transmitted light as a function of the concentration of the suspended particles forms the basis of turbidimetric analysis. This is illustrated in Fig. 15.1.

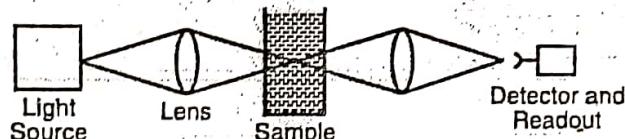


Fig. 15.1

turbidimetry

In nephelometry, the light is also allowed to pass directly through the sample solution having suspended particles. The amount of radiation scattered by the particles is measured at an angle (usually 90°) to the incident beam. The measurement of the intensity of the scattered light as a function of the concentration of the dispersed phase forms the basis of nephelometric analysis. This is illustrated in Fig. 15.2.

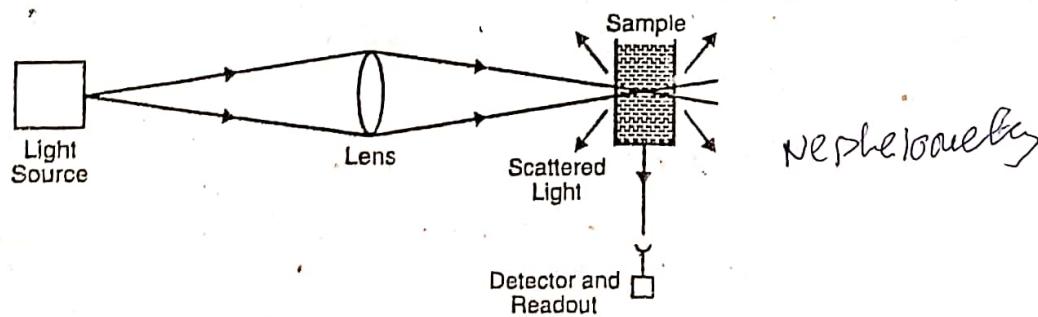


Fig. 15.2

nephelometry

15.2 Turbidimetry and Colorimetry

Turbidimetry is much similar to colorimetry because both involve measurement of the intensity of light transmitted through a medium. But these differ in the sense that the light intensity is decreased by

turbidimetry and by the absorption in colorimetry. Due to this reason both techniques may use similar even identical apparatus.

15.3 Nephelometry and Fluorimetry

Nephelometry is much similar to fluorimetric method because both involve the measurement of scattered light. But the basic difference is that the scattering is elastic in fluorimetry and inelastic in nephelometry. It means that both incident and scattered light are of the same wavelength in nephelometry whereas the scattered light measured in fluorimetry is of a longer wavelength than the incident light.

15.4 Choice Between Nephelometry and Turbidimetry

The choice between a nephelometric and turbidimetric analysis depends upon the amount of light scattered by suspended particles present in the solution. Turbidimetry is satisfactory for determining relatively high concentrations of suspended particles because the scattering is quite extensive due to the presence of many particles. On the other hand nephelometry is most suited when the suspension is less dense and decrease in power of the incident beam is small. In such a case, more accurate results are obtained due to the small amount of scattered light which would be measured against a back background. In such an instance, turbidimetry should not be used since a comparison would have to be made of two large quantities of nearly equal values.

15.5 Theory

(1) Reflection vs. Scattering. Both reflection and scattering phenomena are very important in turbidimetry and nephelometry. If light is allowed to pass through a solution having suspended particles, reflection will take place if the dimensions of suspended particles are larger than the wavelength of incident light. On the other hand, scattering will take place if the dimensions of suspended particles are of the same order of magnitude or smaller than the incident wavelength. This distinction plays an important role in nephelometry and turbidimetry because it affects the sensitivity of the measurement as well as how the measurement is made. This can be seen from the following discussion :

- (i) In nephelometric measurements, the suspended particles should be small with respect to the wavelength used. This is required so that scattering rather than reflection predominates. At the same time, smaller particles undergo scattering to give rise a symmetrical pattern of secondary rays in space having maximum intensity at 90° to the primary incident beam. Due to this reason, most of the instruments used in nephelometry involve measurements at 90° .

If the particles are larger, a small fraction of light gets deviated at right angle to the primary beam whereas the larger fraction gets deviated at angles other than 90° . In such cases, nephelometric measurements are made at angles less than 90° from the primary beam, say in the region 5° to 20° , or even 45° .

In nephelometry, suspended particles should neither be too large nor too small otherwise the scattering efficiency falls off. For measurements to be made in the ultraviolet and visible regions of spectrum the optimum particle size should be in the range of about 0.1 to $1 \mu\text{m}$.

- (ii) In turbidimetric measurements, particles larger than the wavelength of light do not pose much problem because measurement depends on the total radiation removed from the primary beam irrespective of the mechanism by which it is removed or the angle through which it undergoes deviation. But with larger particles another problem arises, i.e., the relationship between absorbance and concentration does not remain linear. Thus, in such cases measurements cannot be very accurate.

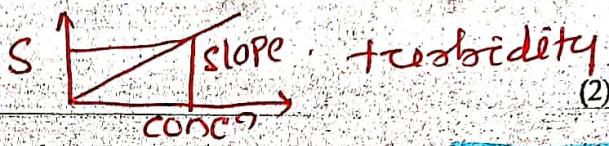
(2) Factors Affecting Measurements. The amount of radiation removed or deviated from the primary radiation beam depends on the following factors :

- (a) Concentration. In turbidimetry, one measures the transmittance of a primary beam of radiation which is defined as follows :

$$T = \text{Transmittance} = \frac{I}{I_0} \quad (1)$$

where I_0 denotes the intensity of incident light after passing through comparison cell containing solvent and I , the intensity of the light after passing through the cell containing the sample solution. The transmittance T is related to the concentration c of suspended material by an equation similar to Beer's law, i.e.,

$$S = \log \frac{I_0}{I} = kbc \quad (2)$$



where S is called turbidance due to scattering (analogous to the term absorbance), b is the path length, and k is proportionality constant known as turbidity coefficient. The value of k depends on the particle size and shape, wavelength and refractive indexes of the suspended and suspending media.

It is important to remark here that equation (2) holds good only for such small particles where Rayleigh's scattering is the main mechanism of attenuation and for dilute suspensions where multiple scattering is unlikely. But the suspension should not be too dilute otherwise the transmitted intensity I becomes equal to the incident intensity. In such a situation accurate measurement is not possible.

Equation (2) shows appreciable departures for real cases in analogous to departures from Beer's law. In turbidimetry, a working curve is prepared by plotting S vs. known concentrations of scattering material and then the unknown concentrations are observed from this curve by knowing their S values from the turbidimeter.

In nephelometry, one cannot relate the scattered intensity to the concentration by any simple theoretical equation. The reason for this is that the scattered intensity in nephelometry depends upon a number of complicated factors like the properties of the scattering suspension and the angle and geometry of the measuring instrument. The best equation will be that one which will relate the scattered intensity I_s to the concentration of suspended particles c by the approximate empirical equation such as

$$\log \frac{I_0}{I_s} = k_s c \quad (3)$$

where k_s denotes the empirical constant for a particular system and I_0 is the incident intensity and all measurements are carried out under identical conditions.

Whenever quantitative analysis is to be carried out in nephelometry, a working curve is obtained by plotting the concentration of suspended particles vs. I_0/I_s under carefully controlled conditions. But in most of the cases $\log(I_0/I_s)$ is plotted vs. c to conform with the more usual spectrophotometric and turbidimetric practices.

- (b) **Particle geometry**—In both turbidimetric and nephelometric analysis, the most critical factor is the control of particle size and shape. The ideal situation is that when all samples and calibration solutions with which they are compared should possess the same distribution of small medium, and large particles. This, in turn, means that one should prepare samples and standards under identical conditions. But this is not a simple task. The conditions include concentration of reactants, temperature, agitation, pH, presence of non-reactants, temperature, the order of mixing of reactants and the time allowed for particle growth. If one does not maintain these conditions, one may get different sized particles which may introduce major error in turbidimetry and nephelometry.
- (c) **Wavelength of incident light**—In turbidimetry, the wavelength of incident light as an important factor. The general practice is to select such a wavelength where the sample solution does not absorb strongly. If the sample solution is colourless, one must use the incident light of the same colour. On the other hand if clear solutions are having dark particles, light in the red or even infrared region must be used where there is maximum absorption.

In nephelometry, absorption is much less of a problem. In such a case, white light is generally used as a convenience.

- (d) **Refractive index difference**—Best results are obtained when there is an appreciable refractive-index difference between the particle and its surrounding medium. Sometimes it is advantageous to change solvents in order to increase the refractive-index differences.

15.6. Comparison of Spectrophotometry, Turbidimetry and Nephelometry

If incoming radiant energy gets impinged upon particles suspended in a medium which is having a refractive index different from that of the suspended particles, the light which strikes the particles is transmitted at angles other than 180° from the incident light. This light is said to be scattered. Nephelometry involves the direct measurement of the scattered light, whereas turbidimetry involves the measurement of the decrease in the intensity of transmitted light (i.e., that which is not scattered) in a suspension. Nephelometry is similar to fluorimetry in that the measurement, in both cases, is made at an angle to the incoming radiant energy, however, the process mechanisms are entirely different. Turbidimetry has been found to be similar to absorption analysis in that the measurement light is at 180° to the impinging light, but again the mechanisms are entirely different.

In most cases the radiant energy which impinges upon and gets absorbed by particles in solution is almost immediately remitted or dissipated as these particles return to their respective stable energy states. If the wavelength of the impinging radiation becomes greater than the particles size (as is usually the case), the emitted radiation is removed by destructive interference and the path of the light beam appears to be unchanged as it passes through the sample. As the wavelength of impinging radiation approaches the particle size the scattered fraction of light becomes greater.

In dilute suspensions the relationship between the impinging power, P_0 , and the exiting power, P , of a parallel beam due to scattering at a particular wavelength is given as follows :

$$\log \frac{P_0}{P} = kbc$$

where P_0 refers to the initial power of the beam, P is the power of the beam after it passes through the suspension, k is a constant (analogous to absorptivity), b is the path length, and c is the concentration.

The extent of scattering which takes place in a suspension has been found to depend upon three factors :

1. the number of particles (concentration)
2. the size and shape of the particles
3. the wavelength of light. Blue light is scattered to a larger extent than is red light.

Nephelometry and turbidimetry measurements are easily made on simple adaptations of a basic spectrophotometer. Figure 15.3 compares spectrophotometry, turbidimetry, and nephelometry processes and instruments. In comparing the absorption spectrophotometer and the turbidimeter, note the only difference is in the sample. In the absorption spectrophotometer the sample is a true solution, while in the turbidimeter it is a suspension. A comparison of the turbidimeter and nephelometer shows that both samples are suspensions but the angles of measurement are different.

The sensitivity of turbidimetric measurements has been greatly increased with the development of a system where a large end-on-detector is placed close to the sample. Scattered light up to angles of 50° may be collected. This is, in reality, a hybrid between the turbidimeter and nephelometer as we have defined them. Fluorimeters may be easily converted to sensitive nephelometers by removing the emission filter (if a filter instrument) or by adjusting the emission monochromator to zero or the same wavelength as the excitation monochromator (if a grating or prism instrument).

15.7 Instrumentation

Much of the instrumentation used in nephelometry and turbidimetry is very similar to spectrophotometric devices as described earlier. Only special features are described here.

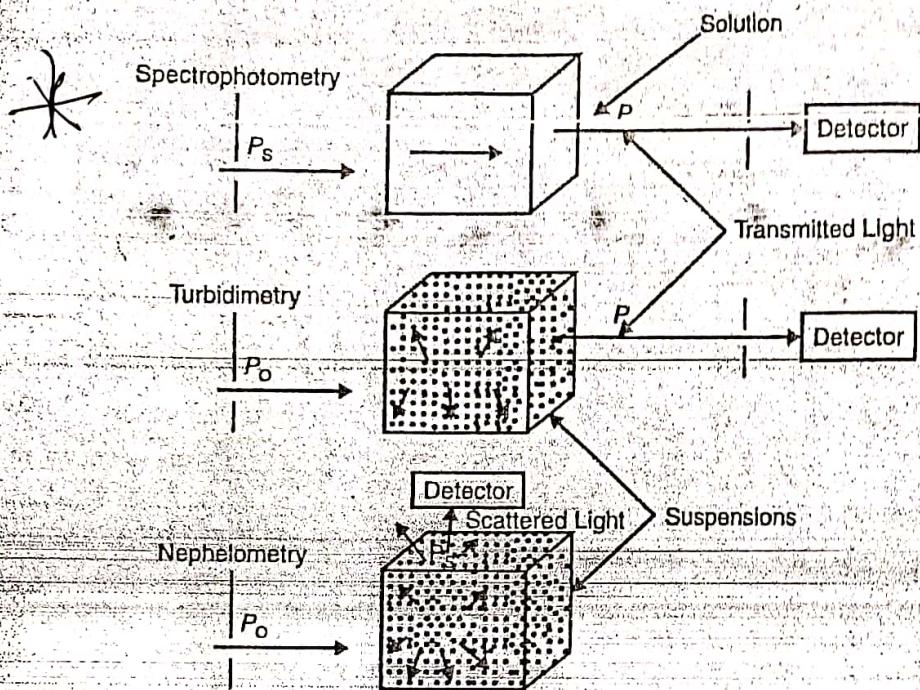


Fig. 15.3 : Comparison of spectrophotometry, turbidimetry, and nephelometry.
 The transmitted light, P_t , is measured in the spectrophotometer and turbidimeter.
 The scattered light, P_s , is measured in the nephelometer.

1. Sources One may use white light in nephelometers but it is advantageous to use monochromatic radiation. Similarly, monochromatic radiation is used in turbidimeters to minimise absorption. In either case it is necessary to use sources providing high intensity monochromatic radiation and wherever possible short wavelengths are used to increase the efficiency of Rayleigh scattering. A mercury arc or a laser, with appropriate filter combinations for isolating one of its emission lines, is undoubtedly the most convenient source. However, if one has to determine the concentration of a particular material, a polychromatic source such as a tungsten lamp may be used. Even in such a case the best results are obtained if we use blue spectral region; a filter may be employed to block other wavelengths.

2. Detectors In nephelometers photomultiplier tubes should be used as detectors because the intensity of scattered radiation is usually very small. In most of the nephelometers, detector is generally fixed at 90° to the primary beam but for maximum versatility and sensitivity it is desirable to vary the detector angle which is generally close to the primary beam. In some nephelometers, the detector is mounted on a circular disc which allows measurement at many angles, i.e., at 0° and from 30° to 135° . The outer edge of the disc is usually, graduated in degree and readable from the outside.

In turbidimeters, ordinary detectors such as phototubes may be used :

3. Cells Although we can use cylindrical cells, they must have flat faces where the entering and exiting beams are to be passed. This is to minimise reflections and multiple scatterings from the cell walls. In general, a cell with a rectangular cross section is preferred. Where measurements are to be made at angles other than 90° , semi octagonal cells (Fig. 15.4) are used. The octagonal faces (Fig. 15.5) will allow measurements to be made at 0° , 45° , 90° or 135° to the primary beam. Generally, walls through which light beams are not to pass are painted a dull black to absorb unwanted radiation and minimise stray radiation. In experimental cells, a blackened curved horn is frequently affixed to the wall directly opposite the entering beam to trap all the beam which is not scattered. Alternatively, one can put a light trap for this purpose in the cell of the chamber in which the cell is located.

4. Turbidimeters In most of turbidity measurements, ordinary colorimeters or spectrophotometers may be used. Simple visual instruments like the Parr turbidimeter or the Duboscq colorimeter can also be

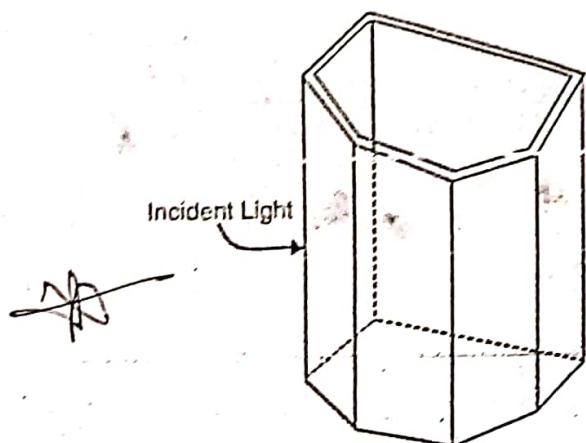


Fig. 15.4

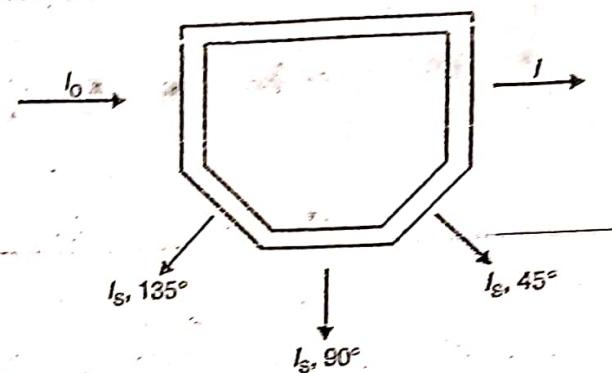


Fig. 15.5

used. But the interesting turbidimeter is Du Pont model 430 which is more sensitive to low concentrations of suspended particles than an ordinary turbidimeter. This model is shown schematically in Fig. 15.6. This is a double-beam instrument which depends for its operation on the relative degree of polarisation of transmitted and scattered light.

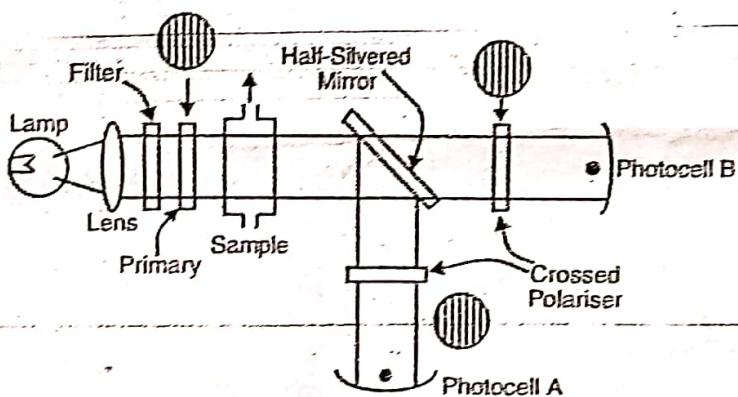


Fig. 15.6

The principle of Du Pont model 430 turbidimeter is that scattering by suspended particles present in solution changes the plane of polarisation of light. The beam of light obtained from the lamp is allowed to pass through the primary polarizer. This causes the incident beam to be plane-polarised. Then, the plane-polarised light is passed through the sample. After passing through the sample, the beam gets splitted up into two parts with the half-silvered mirror and then detected with two separate photocells. When sample solution is not having suspended particles, photocell A shows maximum response whereas photocell B shows minimum or zero response for the sample solutions having suspended particles. The ratio of signal B to signal A is considered to be a measure of the concentration of suspended particles. With the increase in the concentration of suspended particles in the sample, the response of photocell B increases while that of A decreases. Thus, the ratio of two signals is a sensitive measure of the turbidity.

Du Pont model 430 turbidimeter is advantageous to use because it involves the double beam arrangement which minimises the problem of absorption by the particles of the solution. This instrument can be used for the individual samples and also as an on-line monitor for flowing streams. This instrument is insensitive to colour of solvent or of particles or to lamp fluctuations. Du Pont model 430 turbidimeter cannot be used with solutions that contain optically active substances.

Nephelometry and Turbidimetry

Nephelometers—Ordinary fluorimeters are generally used for nephelometric measurements. In some cases spectrophotometers can be employed as nephelometers.

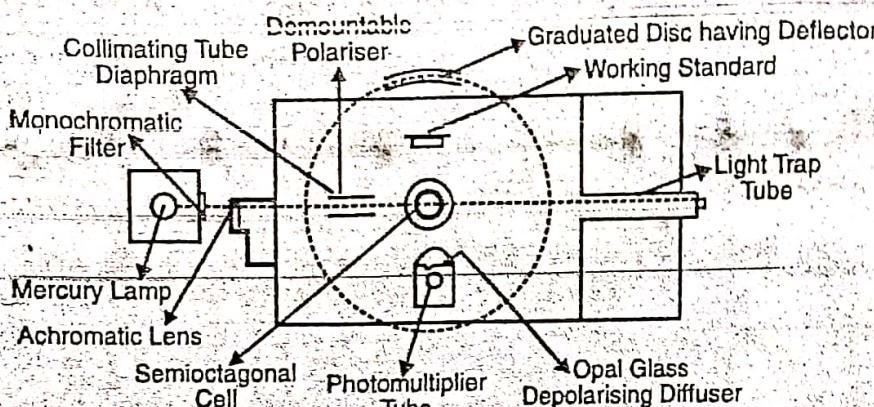


Fig. 15.7

Fig. 15.7 shows a representative precision nephelometer which works at low intensities. The multiplier phototube used as a receiver is mounted on a turnable and may be positioned at any desired angles from 0 to 180° relative to the exit beam. But for the most of nephelometric measurements it is generally positioned at 45° or 90° to the primary beam. The undeviated beam passes into black tube called a light trap.

The nephelometer shown in Fig. 15.7 can be used for the determination of particle size, shape and molecular weight in addition to nephelometric measurements.

A further modification to the nephelometer shown in Fig. 15.7 was suggested by Debye. According to him, the detector and turnable are kept in a closed compartment below the cell. Scattered radiation from the cell is intercepted by a small right-angle prism, also attached to the turnable, and reflected downward to the photomultiplier tube wherever a floor shutter is opened.

15.8 Applications of Turbidimetry and Nephelometry

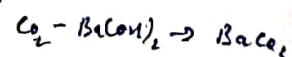
Turbidimetry and nephelometry can be used on gaseous, liquid or even transparent solid samples in greatly varying proportions. The various applications of both these techniques are as follows :

Inorganic Analysis—In some cases, precipitates are difficult to filter due to small size or a gelatinous nature. In such cases, gravimetric operations cannot be performed. In these cases, nephelometry and turbidimetry can be used by converting the precipitates into ideal suspension under rigidly controlled conditions. This is done because the scattering of light depends on the size and number of the particles involved as well as their concentration.

When using nephelometry or turbidimetry for simple quantitative analysis, it is customary to prepare calibration curves from samples of known metal concentrations. The results of suspensions of unknown concentrations are obtained from these calibration curves.

The important uses of nephelometry and turbidimetry are the determination of sulphate as BaSO_4 , carbonate as BaCO_3 , chloride as AgCl , fluoride as CaF_2 , cyanide as AgCN , calcium as oxalate or oleate, and zinc as ferrocyanide. Out of all these, sulphate determination is of particular importance and serves for the routine determination of total sulphur in coke, coal, oils, rubbers, plastics and other organic substances. In order to determine sulphur, it is first of all converted into sulphate. Then it is shaken with sodium chloride solution and excess of solid barium chloride to get a suspension of barium sulphate. Finally this suspension is subjected to nephelometry or turbidimetry as the case may be and the concentration of suspension may be computed from the calibration curve.

Another important application of nephelometry and turbidimetry is the determination of carbon dioxide. The method involves the bubbling of the gas through an alkaline solution of a barium salt and then analyzing for the barium carbonate suspension with nephelometry or turbidimetry.



S
 ↑
 SO₄
 ↓
 NaCl + BaCl₂
 ↓
 BaSO₄

The nephelometric and turbidimetric methods are more precise and sensitive than colorimetric methods. For example, phosphorus can be estimated at a concentration of 1 part in more than 300 million parts of water as a precipitate with strychnine-molybdate reagent. Similarly ammonia at a concentration of 1 part in 160 million parts of ammonia can be detected by adding Nessler's reagent.

The above described methods are widely used in water treatment plants, in sewage works and in power and steam generating plants. In water treatment plants, methods are used in the analysis of water for the determination of clarity and for the control of treatment processes.

Some turbidimetric and Nephelometric methods are given in Table 15.1.

Table 15.1 : Some Turbidimetric and Nephelometric methods

Element	Method	Suspensions	Reagent	Interferences
Ag	T, N	AgCl	NaCl	—
As	T	As	KH ₂ PO ₄	Se, Te
Au	T	Au	SnCl ₂	Ag, Hg, Pd, Pb, Ru, Se, Te
Ca	T	CaC ₂ O ₄	H ₂ C ₂ O ₄	Mg, Na, SO ₄ ²⁻
Cl ⁻	T, N	AgCl	AgNO ₃	Br, I ⁻
Se	T	Se	SnCl ₂	Te
Te	T	Te	NaH ₂ PO ₄	Se

T = Turbidimetric, N = Nephelometric

2. **Organic Analysis**—In food and beverages, turbidimeter is used for analysis of turbidity in sugar products, and clarity of citrus juices. Another interesting application is the determination of benzene in alcohol by dilution with water to make an immiscible suspension.
3. **Biochemical Analysis**—An important application of turbidimetry is to measure the amount of growth of a test bacterium in a liquid nutrient medium. It is also used to find out the amount of amino acids, vitamins and antibiotics. Nephelometry has been used for the determination of protein and the determination of yeast, glycogen and of beta and gamma globulin in blood serum and plasma.
4. **Air and Water Pollution**—Turbidimetry and nephelometry are used for the continuous monitoring of air and water pollution. In air, dust and smoke are monitored whereas in water, turbidity is monitored.
5. **Turbidimetric Titrations**—These titrations may be carried out in a manner analogous to photometric titrations. In these titrations, the absorbance is to be plotted against the volume of titrant added. With the increase in the volume of titrant, the concentration of precipitate increases and hence the absorbance increases. When all the substance gets precipitated, the absorbance becomes constant. Thus, an abrupt change in the slope indicates the end-point. Turbidimetric titrations are shown in Fig. 15.8.

In Fig. 15.8, curve 1 is ideal, curves 2 and 3 might result from precipitates with mixed particle size, poor stirring, etc. In the case of curves 2 and 3, the detection of end point is highly complicated.

Turbidimetric titration can be used in the 10^{-5} to 10^{-6} formal range, with an average relative error ± 5 per cent or more.

In order to carry out turbidimetric titrations, the apparatus required is very simple. It generally consists of a light source and a photocell placed on the opposite side of the titration vessel.

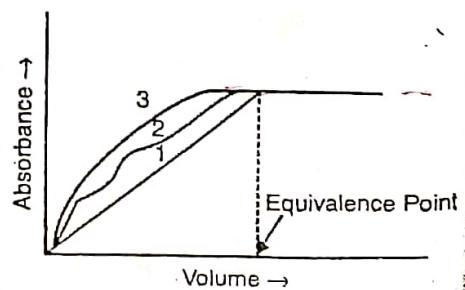


Fig. 15.8

to find volume of titrant required for pptⁿ
complete pptⁿ — constant absorbance

Turbidimetric titrations include the titration of fluoride with calcium, bromide with silver, and sulphate with barium. By turbidimetric titration, silica may be determined in the approximate concentrate range of 0.1 to 150 ppm SiO_2 .

Phase Titrations—Turbidimetry can be used for titrating a mixture of two liquids by a third which is miscible with one but not with the other. Addition of a sufficient quantity of the third liquid will result a separation of phase causing turbidity. In order to interpret the results, one should have knowledge of the three-component phase diagram or one should titrate unknown with known mixtures. In Fig. 15.9, a titration curve is shown for titration of water-pyridine mixture by chloroform.

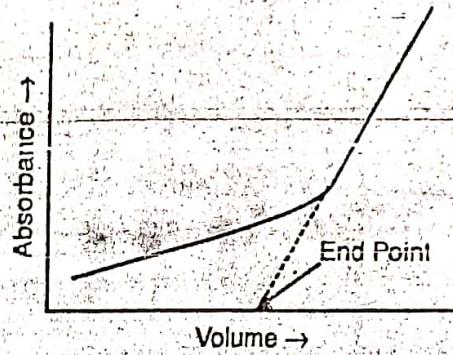


Fig. 15.9

Determination of Molecular Weights of High Polymers

The measurement of the intensity of light scattered by polymer solutions constitutes an important method for determining molecular weights of macromolecules. The turbidity of a sol of macromolecule is related to its molecular weight by the following relation.

$$\text{Limit } \frac{\text{HC}}{\text{Turbidity}} = \frac{1}{M}$$

where H is a constant for a given polymer and a given dispersion medium, C is the concentration of the solution in grams per ml and turbidity is fraction of incident light scattered per cm length of the solution through which it passes. In order to determine molecular weight of a polymer turbidity is measured at different concentrations of its solution in a suitable solvent. The plot of $(\text{HC}/\text{turbidity})$ against concentration is then extrapolated to zero concentration as shown in Fig. 15.10. The intercept gives the value of $1/M$.

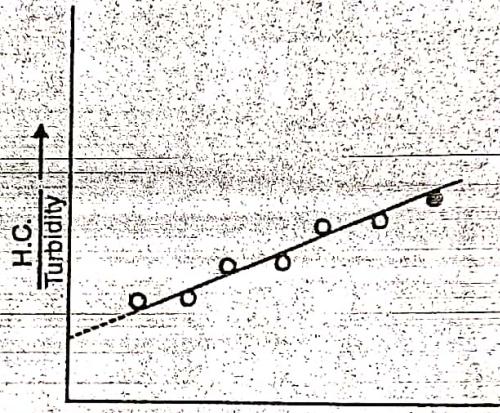


Fig. 15.10

Atmospheric Pollution—Smokes and fogs are visible largely due to light scattering effects. Thus instruments for measuring these effects are very useful in monitoring atmospheric pollution.

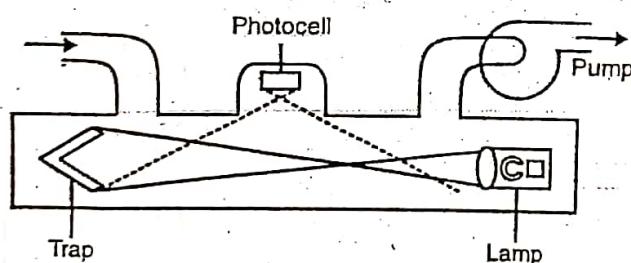


Fig. 15.11 : Nephelometric analyser for atmospheric particulates.

A portable instrument which can be operated in an automobile or air craft is shown in the Fig. 15.11. A beam of light from the lamp is passed through a distance of about 60 cm to a light trap. Air is pulled through this region by a suction pump. A photo cell is situated to one side and baffled so as to receive scattered radiation from the shaded area only.

TEST YOUR KNOWLEDGE

- Q1. Compare the relative sensitivities of the nephelometer and turbidimeter.
- Q2. Compare the nephelometer, turbidimeter and spectrophotometer, as to the type of samples.

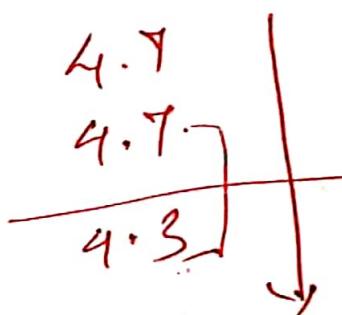
- Q3. Compare the three instruments as to the geometrical arrangements of the samples and detect
- Q4. What is the main criterion for deciding whether turbidimetry or nephelometry should be used in the analysis of a medium containing suspended particles?
- Q5. In the turbidimetric analysis of sulphate using a Beckmann DU spectrophotometer at a wavelength of 355 nm, a certain sample in a 1.00 cm cell is found to have a turbidance S of 9.121. If the turbid coefficient of sulphate is 1.73×10^3 l (mole) (cm) at this wavelength and in this concentration region, what is the concentration of sulphate? (Ans. 6.9×10^{-5} mol)
- Q6. It is important to measure the absorbance of a certain dissolved solute but there is present in the solution a cloudy precipitate of some other solute. Simple means of removing the cloudy solution (filtration, centrifugation) fail. Devise a means of correcting the absorbance for the turbidity, what problems are involved, and how accurate do you think the correction to be?
- Q7. When a nephelometer attachment to a spectrophotometer was used to follow the growth of bacterial species in a synthetic medium at 37°C, the following growth curve data were obtained

Absorbance Readings	0.00	0.12	0.25	0.34	0.50	0.58	0.73	0.84	0.97
Time hours	0.00	0.5	1.0	1.5	2.0	2.5	3.3	3.5	4.0

(a) Plot absorbance vs time on linear paper.

(b) Plot antilog absorbance vs time on linear paper and compare the curve with that obtained in (a).

[(2) A 75% inhibition is equivalent to a 25% bacteria value of the inhibited colony. This corresponds to a concentration of 0.045 mg penicillin per litre.]



5.6
5.2
5.2