2

WATER SAMPLING AND ANALYSIS

Many profound statements can be made about water and its importance in our lives. Its beneficial qualities are many. However, routinely handling large quantities of waters of vastly differing compositions at minimum cost and with a minimum of operating problems often presents some tremendous problems.

CHEMICAL AND PHYSICAL PROPERTIES

Water is often called the universal solvent because it has the power to dissolve virtually all inorganic substances to some extent. In its pure state it has the following physical properties:

TABLE 2.1

Physical Properties of Water

Property	Value
Molecular Weight	18
Density @ 4°C	1 g/mL
Freezing Point	32°F [0°C]
Boiling Point	212°F [100°C]

Most water handling problems in the oilfield arise from the fact that water is such a superb solvent. Both produced waters and surface waters contain considerable quantities of impurities. It has had ample contact with soil and rock formations and has dissolved certain compounds. In addition, it usually contains some suspended solids and dissolved gases. Water will dissolve metal. Microbiological growths often proceed very readily in water. As conditions of temperature and pressure change, many of the dissolved compounds may become insoluble to some degree, precipitate from the water and form scale. The number and combination of difficulties which may arise in water handling are enormous.

In the oilfield we use water for many purposes. The most common are:

* Injection into subsurface formations to increase oil recovery and/or maintain reservoir pressure.

* Injection into subsurface formations to dispose of waste waters.

* Disposal of waste waters into surface waters.

- Cooling of natural gas engine jackets, compressor cylinders, natural gas and other process streams.

- Feedwater for boilers and steam generators.

Regardless of the application, we have two primary goals from an operational standpoint:

- Avoid plugging and deposition of solids in lines, vessels and wells.

- Prevent corrosion of surface and downhole equipment.

WATER SAMPLING

One of the first items of interest in water handling is to sample it and determine its composition. This is our primary means of detecting present and potential problems. However, the water sample must be representative of the water of interest or our analysis will lead to false conclusions. The importance of good sampling practices cannot be overemphasized. An extremely accurate chemical analysis of a water sample, followed by a brilliant assessment of the problems indicated by the analysis, is worthless if the sample does not represent the water in your system.

Sample Containers

Clean (preferably new) plastic bottles with tightly fitting plastic caps are recommended for routine water samples. Pint or quart (500 mL or one liter) bottles are commonly used. Several different types of plastic and different cap designs are available. Once you have selected a particular bottle and cap combination, fill it with water, cap it, and squeeze it to make sure that the cap will not pop off or leak. Wide-mouth bottles are usually easier to fill, but often have less dependable caps.

Label the bottle (not the cap) so that the sample can be identified. Cardboard mailing tubes or cartons should be obtained if the samples are to be shipped to a laboratory or carried a considerable distance.

If the sample is to be analyzed for oil content or for the concentration of any other organic constituent, a glass bottle should be used. Oil or other organic materials will adhere to the walls of a plastic container or be absorbed by it. Extra precautions are necessary in packing the sample for shipment. Freezing can be a problem. Use a plastic cap with a plastic liner.

Never use a metal container or a metal cap. The water will corrode them and become contaminated with corrosion products.

Sample Volume

A minimum sample volume of one pint (500 mL) is recommended for routine analysis.

If you are going to personally perform on-site analyses, you can take as much as you think you need. If only one or two analyses are to be performed, only a few hundred milliliters may be necessary. Also, since you are on site, you can run back to the sampling point and obtain some more water (provided the water system is not changing composition rapidly). But remember that if you send water samples to a laboratory several miles away and you don't send enough to permit them to perform all of the analyses you want, you are simply out of luck. Always send more than enough if there is any doubt in your mind as to the minimum volume required.

Sampling Procedure

If a sampling valve is available, connect a piece of plastic tubing to the end of the valve. A small nipple or hose connector is handy for this purpose. Open the valve and let the water run for at least one minute. Watch to see if the color of the water is changing. If it is, wait until the color becomes constant. Remember that there is probably some debris in the valve or in the bottom of the line and this will have to be flushed out before you can get a good sample.

Once you have a representative water flow, the following sampling procedures are recommended:

- Sample for Routine Analysis — Rinse the bottle out three times, then place the end of the hose in the bottom of the bottle and let the bottle overflow for an estimated 10 volumes. Then slowly pull out the hose and quickly cap it to minimize (1) oxygen contamination and (2) the escape of dissolved gases.

- Sample for Oil-in-Water Analysis — Fill a clean glass bottle to the neck directly from the sample point and cap quickly. Do not rinse or overflow the bottle with the water to be sampled as in the case of the sampling procedure given for routine analyses. Oil will tend to adhere to the bottle wall and separate from the water. If the bottle is filled more than once, oil from each filling is likely to stay in the bottle, giving erroneously high results. Alternately, free oil may be carried out of the bottle by overflowing, giving low results.

- Sample for Bacterial Analysis — This procedure is covered in detail in Chapter 5.

Once the sample is capped, prepare a label immediately and attach it to the bottle or label the bottle with an indelible, smear-proof marking pen. Make sure the label is securely glued to the bottle. You can mark the cap for convenience if you wish, but remember that caps can be inadvertently switched!

If the sample is to be sent to a laboratory for analysis it should be accompanied by a Water Sample Description Form detailing the sampling conditions. A typical example is given in Appendix 5.

Some other hints:

1. Take wellhead samples at the wellhead, not at the heater-treater or at the tank.

2. If a tank is to be sampled, sample it at several levels, preferably top, middle and bottom. This can require special equipment. You may be able to borrow a "thief" from a gauger and clean it thoroughly before use in order to obtain a sample from the center of a conventional tank.

3. Take samples from the system when it is operating normally. It is often most convenient to take samples when the system is shut down. Needless to say, this type of sample is of questionable value. Make sure the flow rate is "normal" and that nothing unusual is going on upstream of the sampling point.

4. If you are sampling a surface water as a possible source for a waterflood remember that the water composition (especially the turbidity, oxygen concentration and microbial population) may change considerably with the time of the year. It is advisable to sample at several points over a period of several months.

5. Waters for disposal may change considerably with time. Plant waste waters may show a cyclic change in composition due to ion exchange regeneration, cooling tower blowdown cycles, or plant cleaning operations. Once again, a series of samples over a period of time is recommended. Conversations with plant personnel may enrich your intuition as to when to take samples which will reflect the greatest variations in disposal water composition. This can influence your water treating procedure.

QUANTITATIVE ANALYSIS OF OILFIELD WATERS

Water analyses are routinely carried out in laboratories by skilled chemists. They are capable of making extremely accurate measurements on the water sample provided. However, many water properties can change very quickly after sampling. Typical are pH, temperature, dissolved gas content, suspended solids and bacterial population. This means that many of the properties which are of greatest concern to us can be determined accurately only by measuring them on-site. Therefore, a thorough analysis of any water usually involves both laboratory and field analyses.

It is extremely important that any person involved in a water injection or disposal project have an understanding of:

- The constituents and properties of water of greatest importance in water systems
- The significance of each
- The analytical methods typically used, along with their strengths and weaknesses

If these items are understood, then it is possible to specify which analyses are needed and to understand the significance of the results.

Primary Constituents and Properties

In water handling operations we are primarily concerned with those ions and physical properties which are important from the standpoint of plugging or corrosion. Table 2.2 is a list of the most important.

It may also be desirable to measure the amount of chlorine (a bactericide) or the concentration of treating chemicals present in order to monitor their effectiveness.

In steam operations and cooling water systems the amount of silica (SiO_2) in the water is also important, as it can form deposits.

TABLE 2.2
Primary Constituents and Properties of Oilfield Waters

Cations	Anions	Other Properties
Sodium (Na^+)	Chloride (Cl^-)	pH
Calcium (Ca^{++})	Sulfate ($SO_4^=$)	Bacterial Population
Magnesium (Mg^{++})	Bicarbonate (HCO_3^-)	Suspended Solids: Amount, size, shape, composition
Iron (Fe^{+++} & Fe^{++})	Carbonate ($CO_3^=$)	Turbidity
Barium (Ba^{++})		Water Quality
Strontium (Sr^{++})		Dissolved Oxygen
		Dissolved Carbon Dioxide
		Total Sulfides as H_2S
		Oil Content
		Temperature
		Total Dissolved Solids (TDS)
		Specific Gravity
		Resistivity (Conductivity)
		Silica

Significance of Constituents and Properties[2.1]

Cations

a. **Sodium** is a major constituent in oilffield waters, but does not normally cause any problems. About the only exception is the precipitation of NaCl from extremely salty brines.

b. The **calcium** ion is a major constituent of oilfield brines and may run as high as 30 000 mg/L although its concentration is normally considerably lower. The calcium ion is of major importance because it readily combines with bicarbonate, carbonate or sulfate ions and precipitates to form adherent scales or suspended solids.

c. **Magnesium** ions are usually present in much lower concentrations than calcium. They tend to **add** to $CaCO_3$ scaling problems by co-precipitating with the calcium ion. It is very common to find magnesium in calcium carbonate scales.

 Magnesium ions **decrease** the amount of $CaSO_4$, $CaSO_4$ and $CaSO_4$ scales. They do so by forming "ion pairs" with the sulfate ion. Essentially, the magnesium ion has the ability to form a compound which remains in solution. The sulfate ions which are tied up with magnesium are not available to form sulfate scales.

d. The natural **iron** content of formation waters normally is quite low and its presence is usually indicative of corrosion. It may be present in solution as ferric (Fe^{+++}) or ferrous (Fe^{++}) ions, or it may be in suspension as a precipitated iron compound. "Iron counts" are often used to detect and monitor corrosion in a water system. The presence of precipitated iron compounds is one of the major causes of formation plugging.

e. **Barium** is of importance primarily because of its ability to combine with the sulfate ion to form barium sulfate, which is extremely insoluble. Even small quantities can present severe problems.

f. **Strontium**, like barium and calcium, can combine with the sulfate ion to form insoluble strontium sulfate. Although more soluble than barium sulfate, it is often found in scales mixed with barium sulfate.

Anions

a. The **chloride** ion is nearly always the major anion in produced brines and is usually present as a major constituent in fresh waters. The major source of the chloride ion is NaCl, so the chloride ion concentration is used as a measure of water salinity.

 Although salt deposition can be a problem, it is normally of little consequence. The primary problem associated with the chloride ion is that the corrosivity of the water increases as it gets saltier. Therefore, high chloride concentrations make corrosion more likely. Also, the chloride ion is a stable constituent and its concentration is one of the easier ways of identifying a water.

b. The **sulfate** ion is a problem because of its ability to react with calcium, barium or strontium to form insoluble scales. It also serves as a "food substance" for sulfate reducing bacteria.

c. The **bicarbonate** ion can react with calcium, magnesium, iron, barium and strontium ions to form insoluble scales. It is present in virtually all waters. Bicarbonate ion concentration is sometimes called methyl orange alkalinity.

d. Like the bicarbonate ion, the **carbonate** ion can also react with calcium, magnesium, iron, barium and strontium ions to form insoluble scales. Carbonate ions are rarely present in

produced waters because the pH is usually too low (< 8.3). Carbonate ion concentration is sometimes called phenophthalein alkalinity.

Other Properties

a. The *pH* is extremely important for several reasons. The solubility of $CaCO_3$ and iron compounds is highly dependent on pH. The higher the pH, the greater the tendency for precipitation.

   As the pH decreases (becomes more acidic) the scaling tendency of the water is decreased, but its corrosivity is increased. Most oilfield waters have a pH between 4 and 8.

   Both H_2S and CO_2 are "acid" gases as they tend to lower the pH of water (make it more acid) when they dissolve in water. They partially ionize when they dissolve and the degree of ionization is reflected by the pH. This is important in predicting their effect on corrosion and suspended solids.

   Since pH values usually change rapidly after a sample is withdrawn from a pressurized system (due to the escape of dissolved acid gases), pH values should be measured immediately after the sample is taken.

b. The presence of *bacteria* may result in corrosion and/or plugging. A more detailed treatment of this subject is given in Chapter 5.

c. The quantity of *suspended solids* which can be filtered from a given volume of water using a membrane filter is one basis for estimating the plugging tendency of a water. A $0.45 \ \mu m$ pore-size filter is commonly used.

d. It is possible to estimate the *particle size distribution* of the suspended solids in a water sample by various techniques. A knowledge of the particle size distribution can be very helpful in determining the need for filtration and in filter selection. It is also useful in monitoring filter performance.

e. Determination of *particle shape* by visual or scanning electron microscopy is very helpful in the determination of filtration needs. It is usually used in conjunction with particle size distributions.

f. Determination of the *composition of the suspended solids* makes it possible to ascertain their origin (corrosion products, scale particles, formation sand, etc.) so that proper remedial action can be taken. Knowledge of their chemical composition is also important from the standpoint of designing a cleanout procedure should plugging occur.

g. *Turbidity* simply means that the water is not "clear" and that it contains undissolved matter such as suspended solids, dispersed oil or gas bubbles. It is a measure of the degree of "cloudiness" of the water. Turbidity indicates the possibility of formation plugging in injection operations. Turbidity measurements are often used to monitor filter performance.

h. *Water quality* is a measure of the relative degree of plugging which occurs when a given volume of water is passed through a membrane filter of a given pore size. A pore size of $0.45 \ \mu m$ is most commonly used. The utility of water quality testing lies largely in its use as a comparative measurement.

i. *Dissolved oxygen* contributes significantly to the corrosivity of a water. Also, if dissolved iron is present in a water, the entry of oxygen into the system can result in the precipitation of dissolved iron as insoluble iron oxides which may result in plugging. Oxygen also facilitates the growth of aerobic bacteria.

j. *Dissolved carbon dioxide* influences the pH, corrosivity and $CaCO_3$ scaling tendency of a water.

k. The presence of *sulfides* in water will increase its corrosivity. Dissolved sulfides exist in water as a mixture of HS^- ions and dissolved H_2S gas at the pH values normally found in oilfield waters, and the total concentration of both species is usually measured and referred to as "total sulfides". It may be present naturally in the water or it may be generated by sulfate-reducing bacteria. If a normally sweet (free of H_2S) water begins to show traces of H_2S, this indicates that sulfate-reducing bacteria are probably at work somewhere in the system busily corroding holes in your piping and vessels. In addition, iron sulfide will be generated as a corrosion product, and it is a very efficient plugging agent.

l. The presence of dispersed or emulsified *oil* in water often presents problems when injecting produced waters.

   Oil in water can cause decreased injectivity in several ways. It can cause "emulsion blocks" in the formation. It serves as an excellent glue for certain solids, such as iron sulfide, thereby increasing their plugging efficiency.

   When water is being injected into an aquifer with no initial oil saturation, oil in the water can be trapped in the pores of the formation rock around the wellbore. This creates an oil saturation, which can reduce injectivity.

   An analysis for oil content should be conducted on any water, regardless of origin. There are many ways in which water can become contaminated with oil.

   When produced water is disposed into surface waters, the concentration of oil in the water is usually limited by government regulation.

m. The *temperature* of the water affects the scaling tendency, the pH and the solubility of gases in water. The specific gravity of water is also a function of temperature.

n. The *total dissolved solids* is simply the total amount of matter dissolved in a given volume of water. It can be calculated by taking the sum of the concentrations of all cations and anions shown on the water analysis report, or it can be measured by evaporating a sample of water to dryness and weighing the residue.

o. *Specific Gravity*

$$Specific\ Gravity = \frac{Density\ of\ Water\ Sample}{Density\ of\ Pure\ Water} \tag{2.1}$$

   Density is simply weight per unit volume. Pure water weighs 1 g/mL or 1000 kg/m³. Thus, a specific gravity greater than 1.0 means that the water sample of interest is more dense, or weighs more than an equal volume of pure water. Since the waters we are interested in contain dissolved solids, they are always more dense than pure water and therefore have a specific gravity greater than 1.0.

   The magnitude of the specific gravity is a direct indicator of the total amount of solids dissolved in the water. Therefore, comparison of the specific gravity of several waters gives a rapid estimate of the relative amounts of solids dissolved in the waters.

   A graph of total dissolved solids as a function of specific gravity is given in Appendix 6. This is an empirical correlation based on actual density measurements of oilfield waters.

   Specific gravity is also a useful check on the accuracy of laboratory water analyses. If the quantity of dissolved solids calculated from the laboratory analysis drastically disagrees

with the amount estimated from the specific gravity correlation, there is a good chance that the analysis is in error.

p. The *resistance* to electrical current flow is a function of the number of ions dissolved in the water. The lower the resistance the higher the concentration of ions dissolved in the water. It is a method of estimating total dissolved solids which is primarily applied to fresh, low TDS waters. Resistivity measurements are much more sensitive to small changes in TDS in fresh waters than specific gravity.

A chart showing the resistivities of sodium chloride solutions as a function of temperature is given in Appendix 7.

q. *Conductivity* values are measured by some laboratories instead of resistivity. Conductivity is the reciprocal of resistivity and can be derived from resistivity values using the following formula:

$$Conductivity\,(\mu mho\,/\,cm) = \frac{1000}{Resistivity\,(ohm-m)} \qquad (2.2)$$

r. *Silica* occurs in most well waters and can be a serious source of scale deposition in cooling waters and in steam boilers. It normally does not present any problems in water injection operations.

Water Analysis Techniques

Summary of Methods Used

Recommended techniques for measuring the concentration of the ions of interest are given in *API RP 45, Analysis of Oilfield Waters.*[2.2] In addition, meters may be used to determine dissolved oxygen or pH; membrane filter analysis will be used to measure the suspended solids.[2.3]

The types of techniques normally used to analyze an oilfield water sample are summarized in Table 2.3.

Chemical Quantitative Analysis

Quantitative analysis is simply the determination of how much of each of the individual constituents are present in a given sample. Three basic types of methods are commonly used to analyze water samples in the field. More sophisticated instrumental techniques may be used in an analytical laboratory.

Titration

An "indicator" is added to the water sample and a standard solution is then added drop-by-drop from a calibrated dispenser until the solution changes color. The point at which the solution changes color is called the *endpoint*. This simply means that you are finished titrating. The volume of standard solution used to reach the endpoint is noted and the amount of the unknown species present is calculated.

A titration is simply a method of determining the concentration of a particular substance in solution by reacting it with a known material. Reactions are used which are known to be complete at a given pH. A pH meter is normally used to detect the end point in the laboratory. However, color indicators (substances that change color at a specific pH value) are used for analyses carried out in the field.

TABLE 2.3

Summary of Analysis Methods

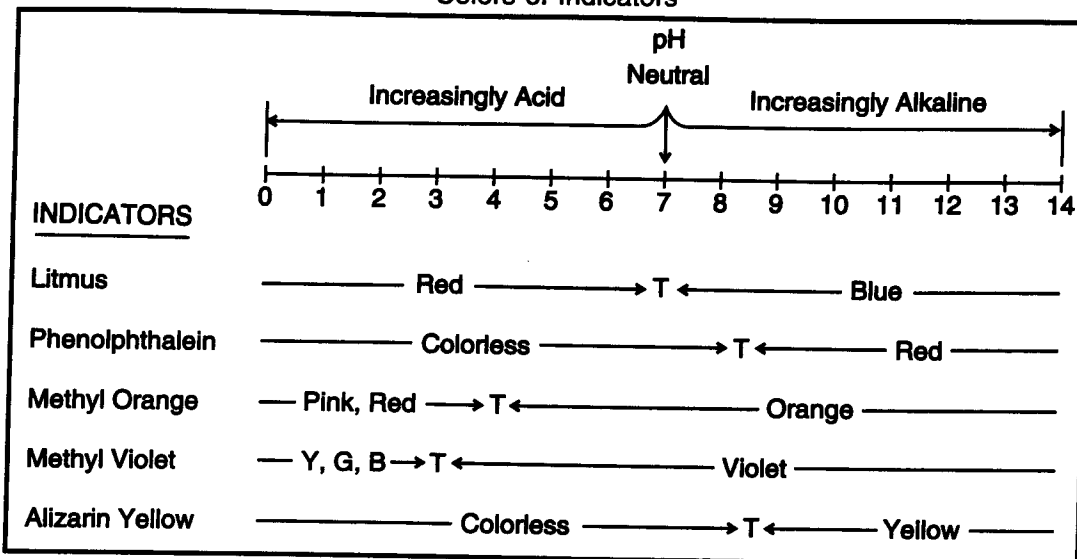| Determination	Analysis Method
Sodium	Calculation, spectroscopic, gravimetric
Calcium	Titration, gravimetric, spectroscopic
Magnesium	Titration, gravimetric, spectroscopic
Iron	Colorimetric, titration, spectroscopic
Barium	Turbidimetric, spectroscopic
Strontium	Spectroscopic
Chloride	Titration
Sulfate	Turbidimetric, gravimetric
Bicarbonate	Titration
Carbonate	Titration
pH	pH Meter, colorimetric, pH paper
Bacterial Population	Culturing, microscopic, others
Suspended Solids Concentration	Gravimetric
Particle Size	Coulter Counter, light scattering, microscopy
Particle Shape	Microscopy
Suspended Solids Composition	Chemical analyses
Turbidity	Turbidimetric
Water Quality	Membrane filter test
Dissolved Oxygen	Oxygen meter, titration, colorimetric
Carbon Dioxide	Titration
Total Sulfides	Alkaseltzer test, colorimetric, titration
Oil-in-water	Colorimetric, spectroscopic, gravimetric
Temperature	Thermometer
Total Dissolved Solids	Calculation, gravimetric, conductivity
Specific Gravity	Hydrometer
Resistivity	Resistivity cell, calculation
Silica	Gravimetric, colorimetric, spectroscopic

The colors of some commonly used indicators are shown in Table 2.4 as a function of pH. The pH value at which the color change occurs is designated with a "T."

An example of a titration is the determination of bicarbonate ion (HCO_3^-) concentration by titration with HCl:

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2$$
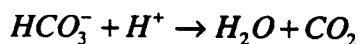
The reaction is complete at a pH of 4.5, so methyl orange is used as the indicator.

TABLE 2.4

Colors of Indicators

INDICATORS	pH scale
	Neutral
	Increasingly Acid — Increasingly Alkaline
	0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
Litmus	——— Red ———→T←——— Blue ———
Phenolphthalein	——— Colorless ———→T←——— Red ———
Methyl Orange	— Pink, Red —→T←——— Orange ———
Methyl Violet	— Y, G, B—→T←——— Violet ———
Alizarin Yellow	——— Colorless ———→T←——— Yellow ———

The concentration of the ion of interest is calculated based on the fact that one equivalent weight of the known, or standard solution, will react with one equivalent weight of the ion in the water sample.

$$E_{standard} = E_{sample}$$

Where: $E_{standard}$ = number of equivalent weights of titrant (standard solution) added to water sample to reach end-point

E_{sample} = number of equivalent weights of ion of interest in water sample

By definition:

$$Normality(N) = \frac{Number\ of\ Gram\ Equivalent\ Weights\ of\ Ion\ (E)}{Liters\ of\ Solution\ (L)} \qquad (2.3)$$

So:

$$[E = N \times L]_{standard} \qquad and \qquad [E = N \times L]_{sample}$$

Setting them equal to each other:

$$[N \times L]_{standard} = [N \times L]_{sample}$$

$$\left[N \times L \times \frac{1000ml}{L} \right]_{standard} = \left[N \times L \times \frac{1000ml}{L} \right]_{sample}$$

$$[N \times mL]_{standard} = [N \times mL]_{sample}$$

$$[N \times mL]_{standard} \times \left[\frac{1}{mL} \right]_{sample} = N_{sample}$$

The normality of the standard solution is known. The volume of the standard solution required to reach the endpoint and the volume of the water sample is measured. The equation can then be solved for the normality of the ion of interest in the water sample. Substituting:

$$\left[\frac{E}{L}\right]_{sample} = N_{sample}$$

$$[N \times mL]_{standard} \times \left[\frac{1}{mL}\right]_{sample} = \left[\frac{E}{L}\right]_{sample}$$

This enables us to calculate the number of equivalent weights of the ion of interest per liter of water. In order to determine the weight of the ion present in a liter, it is necessary to multiply both sides of the equation by the gram equivalent weight of the ion and convert grams to milligrams.

$$[N \times mL]_{standard} \times \left[\frac{1}{mL}\right]_{sample} \times EW(g) \times \frac{1000mg}{g} = \left[\frac{E}{L}\right]_{sample} \times EW(g) \times \frac{1000mg}{g}$$

All of this is the long way to arrive at the final formula which we use to calculate the results from a titration:

$$\frac{[N \times mL]_{standard} \times EW \ of \ ion \times 1000}{mL \ of \ sample} = \frac{mg}{L} \qquad (2.4)$$

The API recommends the use of mg/L as the unit of concentration for water analyses. Therefore, it is suggested that all titration results be reported as mg/liter of the substance determined.

Sometimes ppm are used interchangeably with mg/L. This is correct only when the specific gravity of the water is very near 1.0, since:

$$mg/L = ppm \times S.G. \qquad (2.5)$$

In most titrations certain ions other than the ion of interest will react with the standard solution. This can be a serious problem if the interfering ions are present in significant quantities relative to the amount of the ion of interest present. Table 2.5 lists some common titrations and the interferences for each.
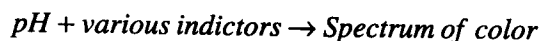
TABLE 2.5

Common Titrations and Interferences[2.2]

Ion	Titrant	Indicator	Interferences
$CO_3^=$	H_2SO_4 or HCl	Phenolphthalein	Borate, silicate, sulfide and phosphate will be included in the values for carbonate and bicarbonate as are volatile fatty acid anions.
HCO_3^-	H_2SO_4 or HCl	Methyl Purple or Methyl Orange	
Ca^{++}	EDTA	Cal-Red, Calcon or Murexide	Barium and strontium are included with the calcium determination. Iron also interferes. Can be masked by triethanolamine when more than 20 mg/L is present.
Mg^{++}	EDTA	Eriochrome Black T	
Cl^-	Silver Nitrate	Potassium Chromate (K_2CrO_4)	Bromides, iodides, thiocyanates, phosphates, carbonates and sulfides precipitate silver ions. Iron, barium, lead, and bismuth precipitate chromate indicator.

Colorimetric Analysis

Colorimetric methods are widely used because of their simplicity. This type of test is based on addition of a material to the water sample which will react specifically with the species in question and produce a colored solution. The intensity of the color is proportional to the amount of the species present. The concentration of the substance in the water is found by comparing the color of the sample with the color standards of known concentration.

For example:

$$Fe^{++} + ortho - phenananthroline \rightarrow Orange\ red$$

$$pH + various\ indictors \rightarrow Spectrum\ of\ color$$

Battery-powered spectrophotometers or colorimeters are also available and can be used for many test procedures. The color-developing reagents are available in pre-weighed packets which are extremely convenient for field use.

One of the most convenient colorimetric analysis procedures employs an extremely clever unitized reagent and sampling system called a CHEMet® (CHEMetrics, Inc., Rt. 28, Calverton, VA 22016). Each CHEMet is a 7-mm diameter glass ampoule with a tapered, prescored tip. Color-forming reagents are sealed inside the ampoule under vacuum. When the user snaps the tapered tip of the ampoule in the sample, vacuum pulls the sample in automatically.
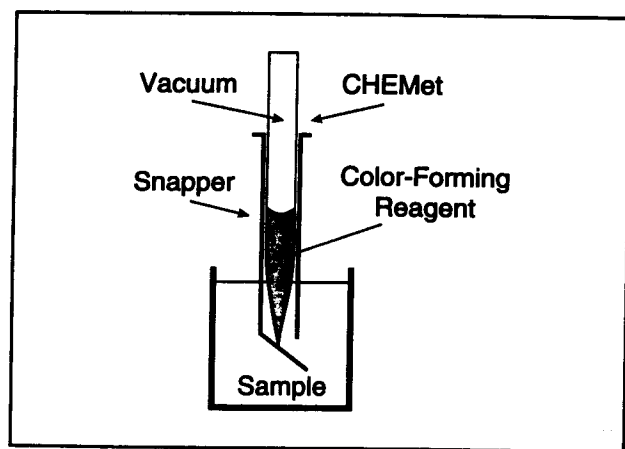
Figure 2.1   Using a CHEMet

Filling is instantaneous and complete except for a small bubble of inert gas. Sample and reagent are mixed by tilting the ampoule and allowing the bubble to travel from end to end several times. After waiting a specified period for color development (usually two minutes or less) the analyst quantifies the result using a color comparator supplied with the kit.

Although CHEMets are available for a fairly wide range of analyses, they have proven to be invaluable for the detection of low levels of dissolved oxygen. Test kits are available with ranges as low as 0-20 ppb (0-0.02 ppm). The results are expressed as mg/L O_2.

The results are not affected by temperature, salinity, other dissolved gases (including H_2S), or the presence of sulfite oxygen scavengers.

Oxidizing agents, such as chlorine, can cause high results unless a special formulation of the reagent is used.

Turbidimetric Analysis

In this type of analysis, a reagent is added to the water which will react with the ion of interest to form a finely divided precipitated solid. The precipitate creates a cloudy solution and the degree of cloudiness, or turbidity, is proportional to the amount of the ion present.

For example, turbidimetric analysis can be used to determine sulfate concentration.

$$SO_4^= + Ba^{++} \rightarrow BaSO_4$$
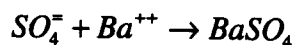
Of the three analytical methods,

- Titration is the most accurate.

- Colorimetric techniques are the most sensitive (can detect the smallest quantities).

- Turbidimetric analyses are the least accurate.

Expression of Results

The concentration of different species in a water can be expressed in several different ways.

1. Milligrams per Liter (mg/L)

   This is the unit of concentration recommended by the API for oilfield waters.

2. Milliequivalents per Liter (meq/L)

   Some laboratories also report results in milliequivalents per liter.

$$meq/L = \frac{mg/L}{Equivalent\ weight} \tag{2.6}$$

3. Parts per Million (ppm)

   If the water is very fresh, the specific gravity is essentially 1.0, and ppm and mg/L are equal. However, as the TDS of the water increases, the specific gravity increases and the units become increasingly different.

$$ppm = \frac{mg/L}{S.G.} \tag{2.7}$$

4. Equivalents per Million (epm)

   This unit of concentration is calculated as follows:

$$epm = \frac{ppm}{Equivalent\ weight} \tag{2.8}$$

5. Grains/U.S. Gallon

   Grains/gallon (gr/gal.) are units which are seldom used in routine oilfield water analysis work. However, they are used in calculations involving water softening by ion exchange.

$$gr/U.S.\ gal. = \frac{mg/L}{17.1} \tag{2.9}$$

6. ppm as $CaCO_3$

   Watch out for this unit system as it is frequently used in cooling water and boiler water work. When the concentration of an ion is expressed in ppm as $CaCO_3$ this means that its concentration has been calculated using the equivalent weight of $CaCO_3$ (50) instead of the equivalent weight of the ion in question. This is done by multiplying the concentration of the ion by the ratio of the equivalent weight of $CaCO_3$ to the equivalent weight of the ion of interest.

For example:

$$ppm\ Ca^{++}\ as\ CaCO_3 = ppm\ Ca^{++} \times \frac{50}{20}$$

$$= 2.5 \times ppm\ Ca^{++}$$

(2.10)

In our work we are usually interested in just the reverse of the above procedure, i.e., converting results reported to us in ppm as $CaCO_3$ to ppm of the ion. Therefore, we do just the reverse of the above.

$$ppm\ Ca^{++} = ppm\ Ca^{++}\ as\ CaCO_3 \times \frac{20}{50}$$

$$= 0.4 \times ppm\ Ca^{++}\ as\ CaCO_3$$

(2.11)

A conversion table for converting ppm as $CaCO_3$ to ppm of the ion is given in Appendix 8.

Calcium carbonate equivalent concentration units are used in water softening calculations and is the standard method of expressing hardness and alkalinity.

7. Hypothetical Salt Combinations

Sometimes the reported results are expressed in ppm of hypothetical salts. The chemist may assume that all of the Ca^{++} present will be present as calcium bicarbonate, $Ca(HCO_3)_2$, for instance. This is not true, since the calcium is present in solution as the calcium ion, not as a salt. Many hypothetical combinations of ions are possible from a single ionic analysis. This unit system is not recommended.

8. Hardness

Total hardness is normally the sum of the calcium and magnesium concentrations expressed as equivalent $CaCO_3$.

$$(ppm\ Ca^{++} \times 2.5) + (ppm\ Mg^{++} \times 4.1) = Total\ Hardness,\ ppm\ as\ CaCO_3$$

(2.12)

9. Alkalinity

Alkalinity in waters is usually attributed to the presence of bicarbonate, carbonate, and hydroxyl ions. However, each of these ions exists only in a given pH range. A general idea of the ions contributing to alkalinity as a function of the pH of the water is as follows:

TABLE 2.6

Ions Causing Alkalinity

pH	Ions Causing Alkalinity
9.6-14.0	OH^- and $CO_3^=$
8.3-9.6	HCO_3^- and $CO_3^=$
4.5-8.3	HCO_3^-

These relationships are not exact, and alkalinity is defined as the capacity of a water to react with hydrogen ions. The distribution of HCO_3^- and $CO_3^=$ ions as a function of pH is shown in Figure 3.1.

Alkalinity is determined by titrating with a standard acid to two different endpoints or pH values.

- **P Alkalinity**: A measure of the number of equivalents of acid required to lower the pH of the water to approximately 8.3 (the phenolphthalein, or "P" endpoint).

- **M Alkalinity**: A measure of the number of equivalents of acid required to lower the pH to approximately 4.5 (the methyl orange or "M" endpoint).

Most natural waters have a pH less than 8.3, and hence have a P alkalinity of zero and contain no $CO_3^=$. This means that they show only M alkalinity, which is attributed solely to HCO_3^-.

Alkalinity and acidity as a function of pH is shown in Figure 2.2.
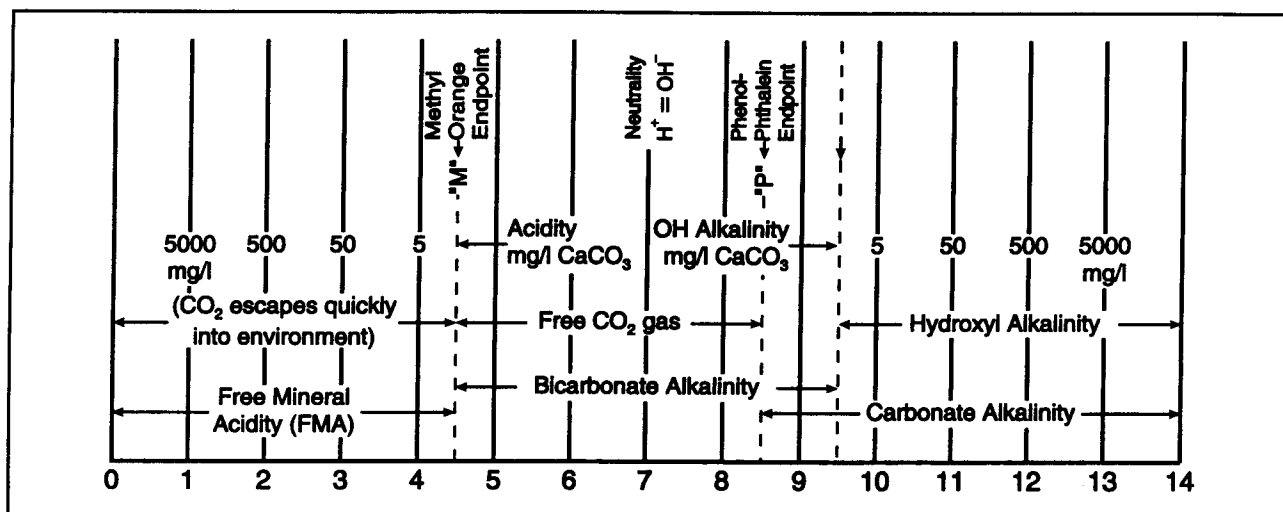
Figure 2.2   Alkalinity and Acidity Ranges

Although absent from surface waters and most aquifer waters, *carboxylic acids* are commonly present in produced waters (water produced with oil and/or gas) and are usually referred to as volatile fatty acids (VFA's). Even though they are classified as acids they are not actually present as acids in produced water because they have ionized to yield a hydrogen ion and a volatile fatty acid anion ("VFA anion").[2.4] For example, in the case of acetic acid:

$$CH_3COOH \rightarrow H^+ + CH_3COO^-$$

Acetic Acid   Acetate Ion
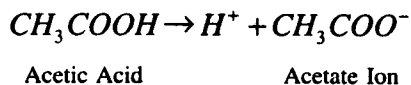
The VFA anions commonly found in produced water contribute to alkalinity and are listed in Table 2.7.

TABLE 2.7

Volatile Fatty Acid Anions

VFA Anions	Formula
Acetate Ion	CH_3COO^-
Propionate Ion	$CH_3CH_2COO^-$
Butyrate Ion	$CH_3CH_2CH_2COO^-$

Alkalinity in produced waters is the sum of the concentrations of the bicarbonate ion and the VFA anions.

$$Alkalinity = HCO_3^- + Acetate + Propionate + Butyrate \qquad (2.13)$$

The acetate ion usually comprises the major portion of the VFA anions in produced waters with considerably smaller quantities of propionate and even smaller concentrations of butyrate ions.

The concentration of the VFA anions in produced water can be substantial relative to the bicarbonate concentration. When this occurs, the bicarbonate ion concentration determined by titration with acid will be significantly in error.

Accurate determination of the HCO_3^- concentration in these types of waters requires the measurement of the VFA anion concentration so that it can be subtracted from the total alkalinity. This measurement is not routinely performed and must be requested if desired. This can be quite important when making calcium carbonate scaling calculations.

Graphical Presentation of Results — Water Patterns

Water analyses are often expressed graphically. The diagram, or pattern, obtained by graphically plotting the results of a water analysis will often highlight important points about the analysis that might be missed by simply reading the report. Pattern comparison is also an easy way to quickly spot differences in two or more waters.

There are many different water analysis diagrams in use. However, the Stiff Method[2.5] has been adopted by the API and is probably the most universally used method in the oilfield. It is the only one presented here. A logarithmic plot of meq/liter of the various ions is most often used, although linear plots are also used. The concentrations of Na^+, Ca^{++}, Mg^{++}, Fe (total), Cl^-, HCO_3^-, $SO_4^=$ and $CO_3^=$ given in Table 2.8 are plotted as shown in Figure 2.3.

TABLE 2.8

Water Analysis

Ion	mg/L	meq/L
Na^+	93230	4053
Ca^{++}	5173	258
Mg^{++}	620	51
Fe (Total)	12	0.6
Cl^-	153175	4320
HCO_3^-	195	3
$SO_4^=$	1910	40
$CO_3^=$	0	0

The concentrations of the cations are plotted to the left of the center line, while the anion concentrations are plotted to the right of the center line.
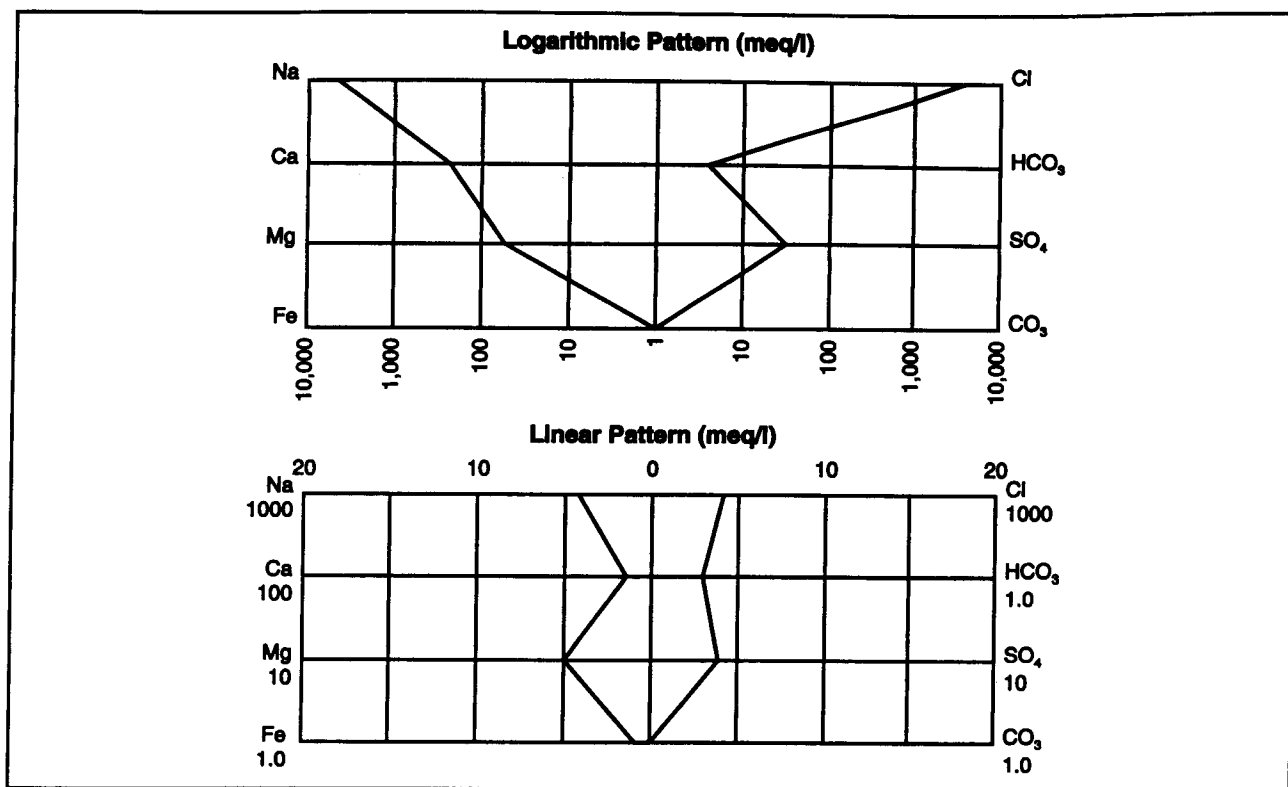
Figure 2.3   Graphical Presentation of Water Analysis — Stiff Method

Water Analysis Reports

Appendix 9 contains examples of two water analysis reports. The first is presented on a modified API Water Analysis Report form. The second report presents the same data in a slightly different format used by a commercial water analysis laboratory.

Both reports contain the following:

- Sample identification information.
- Quantitative analysis of water sample. The degree of detail will vary.
- A graphical representation of the analysis — a water pattern.

The Stiff Method is used in both cases, although the logarithmic pattern is used in the first form while the linear pattern is used in the second.

The API report form is recommended for your own field analysis work. You may find it desirable to eventually modify the form to contain space for reporting additional information pertinent to your own operation.

Oil-in-Water Analysis

The oil content of a water depends on how it is measured. There is no absolute value.

Produced water contains both dispersed oil and "dissolved oil". The dissolved oil consists of hydrocarbons, phenols, organic acids, and low molecular weight aromatic compounds such as benzene and toluene.

Normal oil/water separation equipment cannot remove dissolved organic compounds. However, values of "oil and grease" include **both** the dispersed oil and dissolved organic compounds. Hence, equipment performance should not be judged by "oil and grease" values.

Oil and Grease

In the determination of oil and grease, an absolute quantity of a specific substance is not measured. Rather, the amount of substances with similar physical characteristics are determined quantitatively on the basis of their common solubility in freon. Oil and grease may include hydrocarbons, fatty acids, soaps, fats, waxes, oils, and any other material that is extracted by the solvent from an acidified sample unless it evaporates during the test procedure. Oil and grease is defined by the method used for its determination.

Gravimetric: EPA Method 413.1

The water sample is acidified to a low pH (< 2). The acidified water sample is then poured into a glass container along with freon (fluorocarbon-113) and shaken vigorously. Any oil and grease present is extracted from the water into the freon. The freon is then evaporated from the extract at 70°C, and the residue (oil and grease) is weighed. The results obtained include both dispersed oil and dissolved organic compounds. Any hydrocarbons which will evaporate at this temperature are lost.

Infrared: EPA Method 413.2

The water sample is acidified to a low pH (< 2) and extracted with freon (fluorocarbon-113) as in the gravimetric technique. The freon extract is then placed in an infrared spectrophotometer and the infrared absorption is measured at a wavelength of 2930 cm^{-1}. This wavelength is characteristic of the carbon-hydrogen bond. The oil and grease content of the sample is obtained by comparing the measured value with standards prepared using the same oil. The results obtained include both dispersed oil and dissolved organic compounds.

Results obtained by this method are usually considered to be a more accurate reflection of the true oil and grease content of the water than gravimetric results since the sample is not heated and the loss of light ends is minimized.[2.6]

Petroleum Hydrocarbons

Petroleum Hydrocarbons: EPA Method 502 E

The water sample is acidified to a low pH (< 2) and extracted with freon (fluorocarbon-113) as in the gravimetric technique. The freon extract is then mixed with silica gel. Water soluble polar organic materials are removed from the freon by adsorption on the silica gel. Petroleum hydrocarbons remain in the freon and can be determined by either the gravimetric or infrared methods.

Oil Content by Colorimetric Analysis

The water sample is **not** acidified. Oil is extracted from a water sample using a dense solvent such as trichloroethane. The color intensity of the extract is compared with standards prepared with the same oil to determine the concentration.

This is a very useful field technique and is commonly used to assess equipment performance; however, the sensitivity of the method is limited with light colored oils such as condensates.

Suspended Solids Analysis

Techniques for suspended solids determination and characterization are not covered in API RP 45.[2.2] Because of the extreme importance of suspended solids control in water handling operations, a brief summary of techniques used to determine the amount and nature of suspended solids in a water is presented in the following sections.

Suspended Solids Concentration

The concentration of suspended solids in a water is determined by passing a known quantity of water through a membrane filter and determining the weight of solids collected on the filter. The weight of solids collected (mg) divided by the quantity of water passed through the filter (liters) gives the suspended solids concentration in mg/L. Standard methods for this test are given in NACE Standard TM0173-92 published by the National Association of Corrosion Engineers.[2.7]

It is strongly recommended that water be flowed *directly from the system* through the membrane, when possible, as shown in Figure 2.4. This approach eliminates problems of secondary precipitation associated with sample aging and contact with atmospheric oxygen.
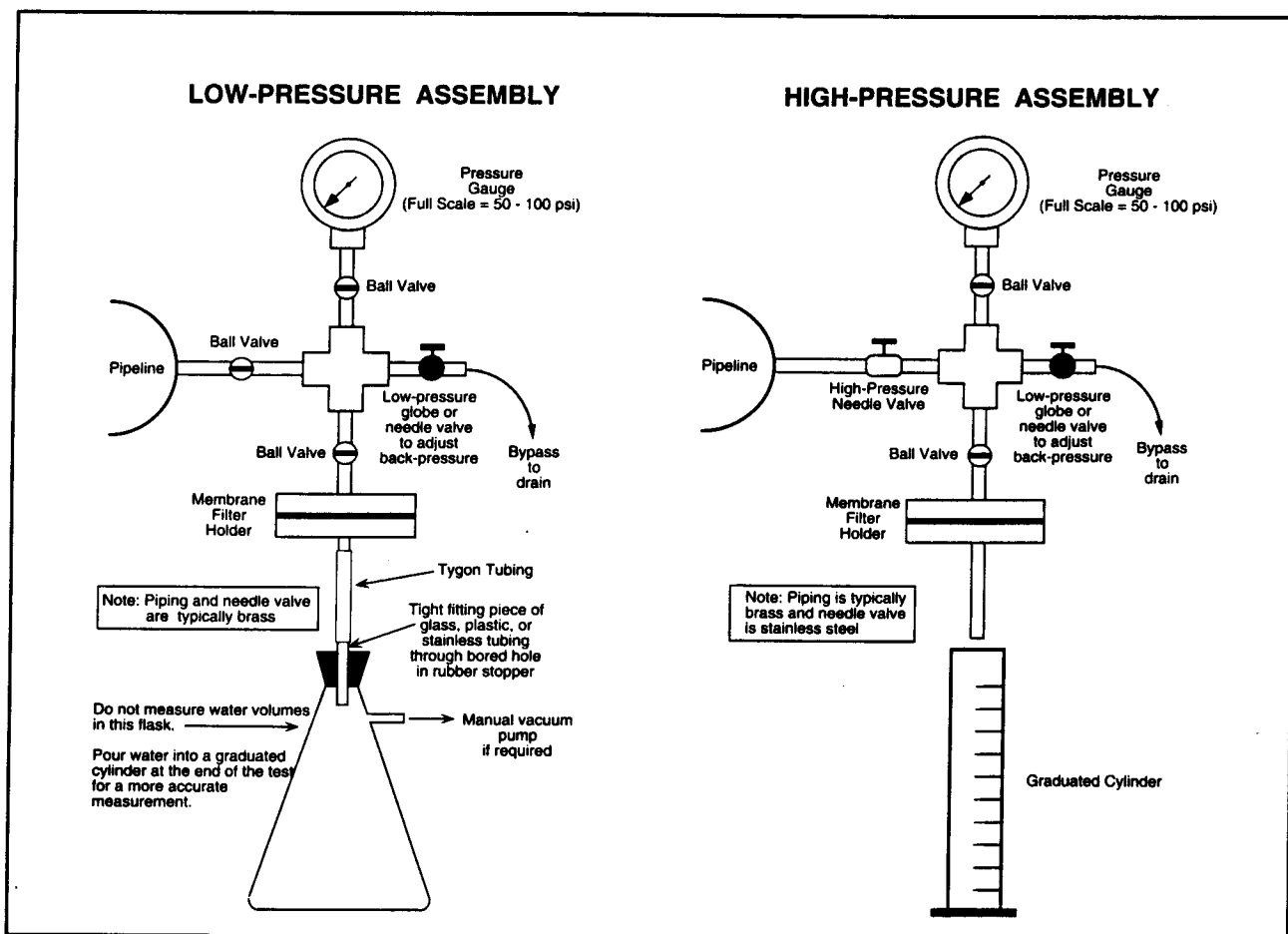
Figure 2.4   Membrane Filter Test Apparatus

Suspended solids are sometimes collected by flowing a water sample from the system into a clear plastic cylinder which has been purged with nitrogen or some other inert gas. Water is then displaced from the cylinder through a 0.45 μm membrane filter by applying approximately 20 psi pressure to the

cylinder with a nitrogen bottle. This method is often used at low-pressure sample points although it is sometimes used at high-pressure sample points as well.

The use of a pressurized plastic cylinder may give acceptable results in some waters but it is not recommended for general use. It is particularly unreliable for produced waters. The basic problem arises from the fact that a large volume of water is transferred from the system into the plastic cylinder (typically several liters) but only a small portion of the water (often a few hundred milliliters in poor quality waters) passes through the membrane filter before it plugs and flow ceases. Two things typically occur:

1. Oil tends to rise to the surface of the water and to coat the walls of the plastic cylinder. The net result is that the amount of oil passing through the membrane filter is less than occurs when the sample is drawn directly from the system. This effects the permeability of the filter cake and hence the volume of water which will flow through the cake at a given pressure drop.

2. Suspended solids tend to segregate in the cylinder, with the larger particles settling to the bottom. This gives a non-representative sample.

Although this technique is widely used, and is indeed a NACE-recommended *alternate* method, we strongly recommend that suspended solids be collected directly from the system using an apparatus such as one of those shown in Figure 2.4.

The most common reason for using the pressurized cylinder method is that system pressure becomes irrelevant. Furthermore, the pressure drop across the membrane filter is always the same, which is very handy when water quality testing (flow rate vs. cumulative volume at a constant ΔP) is performed. A pressure drop of 20 psi is typically chosen because it is the value recommended by NACE for water quality testing.

However, the pressure drop across the membrane filter is not important when the sole purpose is to determine the suspended solids concentration in the water. If the pressure at the sample point is low, the pressure drop across the membrane filter can be increased by using a hand-operated vacuum pump as shown in Figure 2.4.

The test is normally conducted using a single pre-weighed membrane filter when the suspended solids content is 1 mg/L or greater. When the concentration is less than 1.0 mg/L, matched weight membranes or pre-weighed pairs are preferred.

It is critical that the increase in weight of the membrane filter due to solids filtered from the water be sufficient to provide analytical accuracy. For example, a 47-mm diameter, 0.45 μm pore size, membrane filter weighs about 100 mg. At least 2 mg of solids should be filtered from the water so that the weight gain will be at least 2%. This means that the suspended solids concentration determines the amount of water which must be filtered to provide the minimum weight gain required.

Elution Loss

There is one complicating factor when large quantities of water are passed through the standard cellulose acetate/cellulose nitrate membrane filter: the water dissolves a small amount of the filter, resulting in a small loss of weight. This weight loss is referred to as *elution loss*. This loss is not significant when the amount of solids collected on the filter is large. However, elution loss can be quite significant in waters containing low levels of suspended solids.

It has been common practice to deal with this problem by running matched-weight filters. Filtration through two matched-weight membrane filters mounted in series subjects both filters to the same

elution loss but all solids are collected on the top filter. Therefore, the differential weight is the suspended solids corrected for elution loss.

However, it is not necessary that the two filters be matched in weight. If both are pre-weighed, the elution loss correction can be determined from the bottom filter and applied to the top filter.

Another option is to use a different membrane material, such as polyvinylidene difluoride (PVDF) which is not subject to elution loss.

Chemical Composition of Suspended Solids

An analysis procedure for the determination of solids composition is given in TM0173-92.[2.7] Determination of hydrocarbon solubles, acid solubles, organics and insoluble residue should be supplemented by chemical analyses to identify the major components of each fraction. Of specific interest is iron, sulfate and carbonate, supplemented by determinations of calcium, barium, and strontium as deemed necessary. Analysis for silica and protein may also be of interest.

When membrane filters are used in brines, the membrane must first be washed with deionized water prior to weighing and analysis. The purpose of the wash is to remove water-soluble salts which precipitated in the filter when the water evaporated from the wet membrane during drying. They are not a part of the suspended solids.

A typical analysis format for suspended solids is shown in Table 2.9.

TABLE 2.9

Analysis of Suspended Solids

Component	mg/L	mg/L
Total Acid Solubles		1.50
Calcium as $CaCO_3$	0.13	
Iron as FeS	0.40	
Unidentified	0.97	
Total Organics		3.55
Solvent Soluble (Oil)	1.70	
Ignition Loss	1.85	
Total Acid Insolubles		0
Total Suspended Solids		5.05

Water Quality

In water injection systems, water quality is a measure of the relative degree of plugging which occurs when a given volume of water is passed through a membrane filter of a given pore size. A pore size of 0.45 μm is most commonly used.

The National Association of Corrosion Engineers has approved a standard method for running the test.[2.7] Several modified methods are used. However, the basic test consists of forcing a given volume of water through a filter under constant pressure. The cumulative volume through the filter is recorded as a function of time, and the flow rate for each time increment is calculated from the data. Flow rate is plotted versus cumulative volume throughput on a semi-log plot. The slope of the line indicates the "quality," or degree of plugging which occurred with that particular water sample, as illustrated in Figure 2.5.
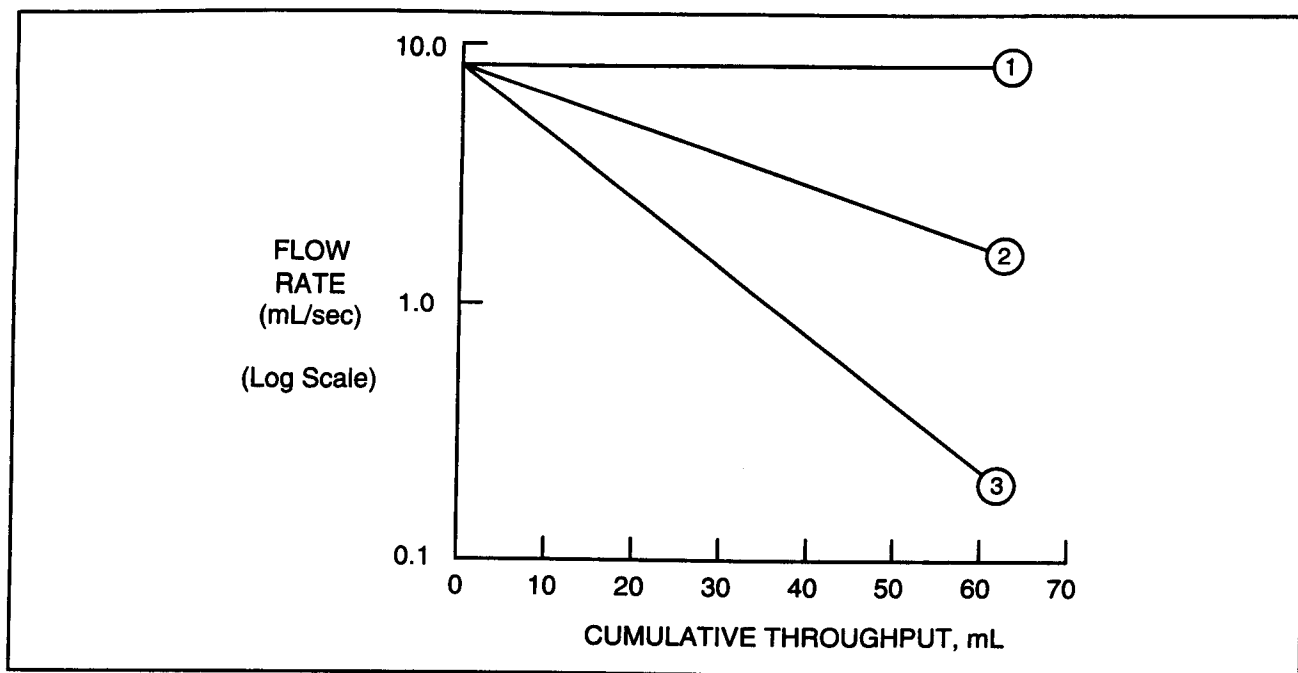
Figure 2.5 Water Quality Plot

It is also a measure of the permeability of the filter cake formed on the membrane. The steeper the slope, the less permeable the cake formed by the solids.

The important point to be made about water quality testing is that it is a way of comparing the relative tendency of different waters to plug a membrane filter. It does not necessarily have any correlation with the tendency of a water to plug the formation.

TABLE 2.10

Interpretation of Water Quality Curves in Figure 2.5

Curve	Quality
1	Excellent. No plugging occurred since the flow rate remained constant throughout the test.
2	Poorer than Curve 1. The flow rate decreased as the cumulative volume throughput increased indicating plugging of the filter.
3	Poorest of the three curves. The flow rate dropped much more rapidly indicating faster plugging.

The utility of water quality testing lies largely in its use as a comparative test.

• Water quality testing can be used to detect changes in a single water at a given point in a system over a period of time.

• Tests can be run at various points through a system to detect changes which may be occurring between the water source and the injection wells.

• Different waters can be compared.

• Through experience, minimum water quality standards may be set for a specific area. Careful correlation of water quality measurements with injectivity data can be very helpful in determining filtration requirements.

Any insoluble material in a water will reduce its quality. Corrosion products, water-formed scales, clay, silt, oil, insoluble treating chemicals, bacterial growths or algae will all contribute to decreased quality.

It should be obvious that the quality required will be largely determined by the reservoir permeability. Tight, low permeability zones will require better water than a high permeability reservoir. What is considered acceptable quality in one area (or zone) might quickly plug a different formation.

Cerini Slope Measurements

In 1953, William F. Cerini proposed a novel means of measuring the slope of water quality curves.[2.8] Although he used a sintered glass disc rather than membrane filters for his test work, his slope measurement technique is still widely used in water-quality work.

The water quality data is plotted in the normal way on two cycle semi-log graph paper. A best fit straight line is drawn through the points, and the slope is then measured as though it were a linear Cartesian plot.

Both the vertical and horizontal components of the slope are measured using the same linear scale. The slope value is then calculated by dividing the vertical component (y) by the horizontal distance (x). As long as the curve slopes downward to the right, the slope value is always negative, and is commonly called the Cerini Slope.

The Cerini Slope of the curve shown in Figure 2.6 is $-2.4/1.5 = -1.6$.

Cerini Slope values are a function of scales used on both the ordinate and the abscissa. Therefore, slope values can be compared only when the scales are fixed.

Relative Plugging Index

Amoco developed a method of rating water quality called the Relative Plugging Index, or RPI.[2.9]

$$RPI = TSS - MTSN \tag{2.14}$$

Where: TSS = Total suspended solids, ppm
MTSN = Millipore test slope number

Millipore Test Slope Number (MTSN)

The MTSN is the Cerini Slope of a conventional water quality curve, with fixed ordinate and abscissa scales:

Vertical "y" axis (Ordinate): 1 cycle/5 inches

Horizontal "x" axis (Abscissa): 500 mL/inch

The MTSN is determined as follows:

1. Plot the water quality data, log flow rate (mL/sec) vs cumulative volume (mL), on 2-cycle semi-log graph paper.

2. Draw a best fit straight line through the data points in the latter portion of the curve as illustrated in Figure 2.6.

3. Select two points on the curve. The coordinates of the selected points are designated as (Q_a, V_a) and (Q_b, V_b).

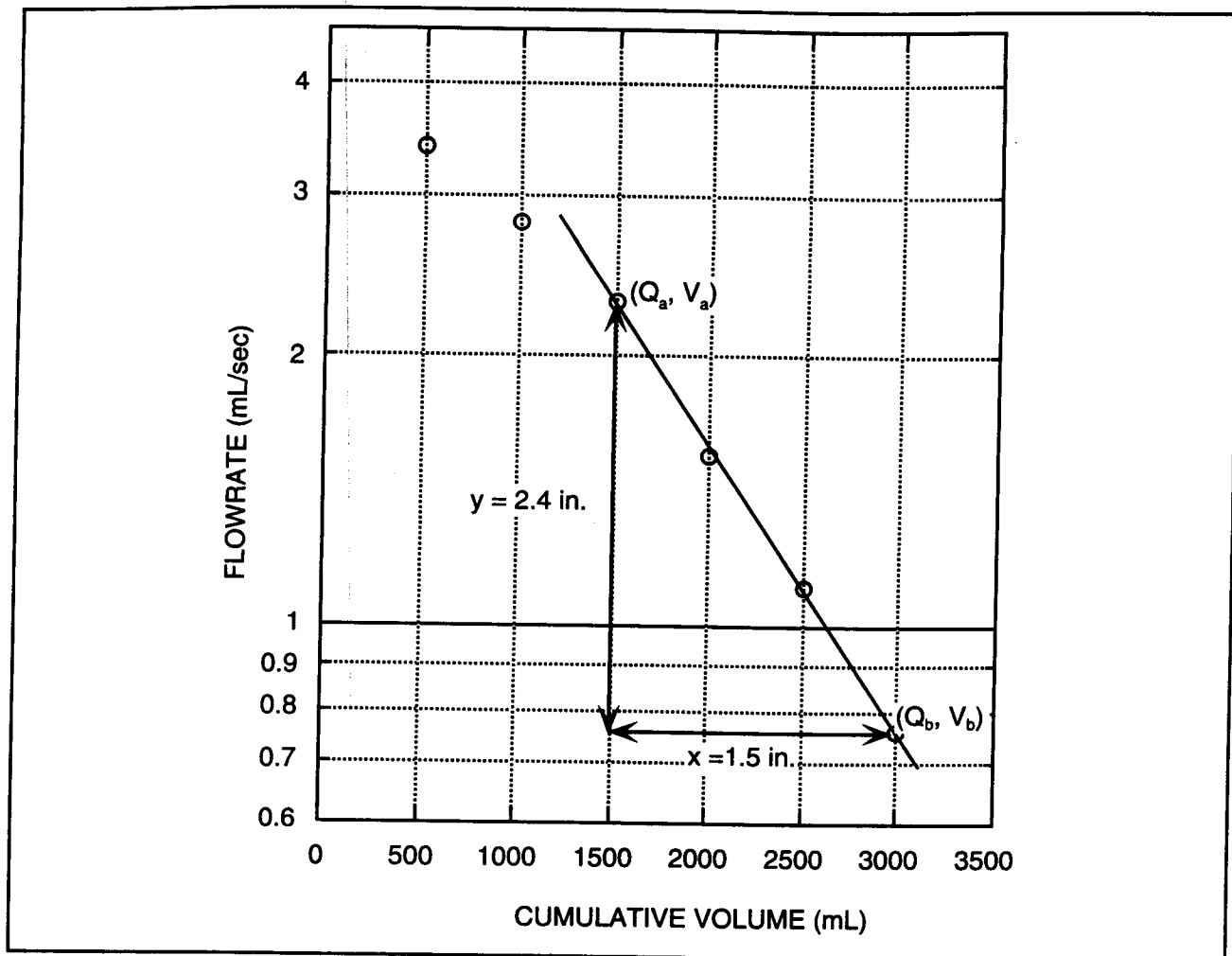4. Calculate MTSN directly from the data or determine it graphically.

Figure 2.6 Measurement of Cerini Slope

The simplest way to determine the MTSN is to calculate it using the following equation:

$$MTSN = \frac{2500\log(Q_a/Q_b)}{V_a - V_b}$$

(2.15)

Use of this equation permits you to use any ordinate and abscissa scales you choose.

If you wish to determine the MTSN graphically, it is necessary to use graph paper with an ordinate scale of 1 cycle/5 inches, which is usually quite convenient, since that is the normal grid size on 2-cycle semi-log graph paper (8-1/2 × 11 sheet).

There are two options regarding the abscissa scale:

1. Use an abscissa scale of 500 mL/inch.

2. Use an abscissa scale other than 500 mL/inch and calculate the equivalent distance on a 500 mL/inch scale using the following formula:

$$x\,(inches) = \frac{V_a - V_b}{500\,mL/inch}$$

(2.16)

MTSN is determined graphically as follows:

1. Measure the vertical distance between Q_a and Q_b, y.
2. Measure the horizontal distance between V_a and V_b, x. If the scale on the horizontal axis is other than 500 mL/in., calculate the difference between the two volumes in milliliters, and divide by 500 to obtain the correct value of x in inches.
3. $MTSN = \dfrac{-y}{x}$ The MTSN is always negative.

Example 2.1:   Given the water quality data in Table 2.11:

The data is plotted in Figure 2.6. The MTSN of the water quality curve is calculated as follows:

$$MTSN = \frac{2500 \times \log(2.3/0.76)}{1500 - 3000} = \frac{2500 \times 0.48}{1500} = -0.8$$

The MTSN can also be determined graphically:

1. y = 2.4 inches

2. $x = \dfrac{3000mL - 1500mL}{500\,mL/inch} = 3.0\ inches$

3. $MTSN = \dfrac{-y}{x} = \dfrac{-2.4}{3.0} = -0.8$

TABLE 2.11

Water Quality Data

Flow Rate (mL/sec)	Cumulative Volume (mL)
3.40	500
2.90	1000
2.30	1500
1.55	2000
1.10	2500
0.76	3000

Water Quality Rating Guide

A water quality rating guide proposed by Amoco is given in Table 2.12.[2.9]

Well Impairment Prediction

Another approach to the presentation and interpretation of water quality data was developed by Barkman and Davidson.[2.10] They developed methods and theory which can be used to interpret water quality data obtained with membrane filters or cores to predict well impairment from suspended solids.

Although this method can be used to make relative predictions, the calculated half-life values have proven to be unreliable in practice.

TABLE 2.12

Water Quality Rating Guide

RPI	General Quality Rating
< 3	Excellent
3-10	Good to Fair
10-15	Questionable
> 15	Poor

Particle Size Analysis

Solid particles found in injection waters range in diameter from less than one micron up to several hundred microns. Figure 2.7 shows the diameters of some commonly encountered particles for comparison.
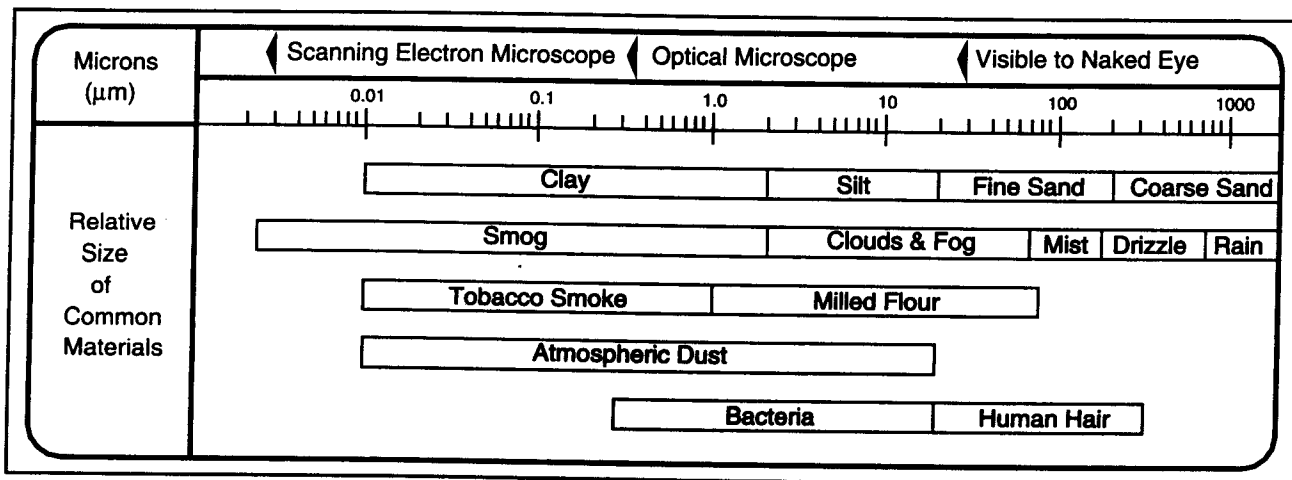

Figure 2.7 Typical Diameter of Common Particles

Although many of the particles found in injection waters are approximately spherical, many are not.

The description of the "size" of a non-spherical particle is one of the fundamental problems of particle technology. The most common approach is to describe the particle by a sphere which will have at least one property in common with it. Thus, a single particle may have several "equivalent sphere sizes" depending on the method used for its measurement, as shown in Table 2.13.

Note that for the particle shown the "diameter" varies by more than a factor of two among the various measurement techniques.

There are a number of techniques which are used to determine the size of particles suspended in water. They are compared in Table 2.14 and discussed in the following paragraphs.

Microscopic Techniques

The use of visual microscopy is probably the oldest technique used to examine particles in oilfield waters. However, it is a rather tedious way to measure particle size distributions, as many particles must be examined if the distribution determined is to be statistically valid. It is more generally used to determine the shape and nature of the particles and to get some idea of their general size range.

TABLE 2.13

Diameters Used for Particle Characterization[2.11]

METHOD OF MEASUREMENT	KIND OF "DIAMETER" MEASURED	EQUIVALENT SPHERES	DIAMETER VALUE ANY UNITS
	True Particle		$d \times h \times w = 1 \times 1 \times 2$
Microscope	Projected-Area Diameter		$d_a = 1.58$
Microscope	Maximum Feret[a] Dia.		$d_f = 2.23$
Sedimentation	Stokes Diameter[b]		$d_{st} = 1.43$
Coulter Counter	Volume Diameter		$d_v = 1.55$
Sieve	Mesh-Size Diameter		$d = 1.00$
HIAC Counter	Surface-Area Diameter		$d = 1.77$

[a] Maximum distance between parallel tangents.

[b] Stokes diameter is included in the expression $3\pi\mu d$, which is the force (resistance to motion) exerted on a particle.

Scanning electron microscopy (SEM) is a popular method of particle examination. Much higher magnifications are possible than with conventional microscopy, and the depth of field is far superior.

Figure 2.8 is an SEM photograph of suspended solids filtered from Aegean seawater, while Figure 2.9 is an SEM photo of solids filtered from North Sea Water.

Both waters contained virtually identical concentrations of suspended solids, but the shapes and types of particles were quite different.

Coulter Counter

Two electrodes are immersed in a beaker of the water of interest, which must contain sufficient dissolved ions to easily conduct electrical current.

The negative electrode is located inside a glass tube which is sealed except for a tiny hole or orifice on the side of the tube. The positive electrode is located in the water sample beaker. (Figure 2.10)

A constant electrical current is passed from the positive electrode to the negative electrode through the orifice. When a non-conductive particle passes through the orifice it causes a change in electrical resistance between the two electrodes which is proportional to the volume of the particle.

TABLE 2.14

Comparison of Commonly Used Particle Analysis Techniques

Technique	Approx Size Range	Sample Requirements	Data Produced	Instrument Portability	Maximum Magnification
Visible Light Microscope		Usually filtered solids on surface of membrane filter although drops of water can be examined.	Particle shape and size.	Easily portable. Requires AC power for illuminating lamp.	800 x (Dry objective) 1500 x (Oil immersion)
Scanning Electron Microscope		Filtered solids on surface of membrane filter. Must be plated with Au or Pd prior to examination. Sample examined under vacuum.	Particle shape and size.	Permanent laboratory installation.	100 000 x
Coulter Counter	0.5 µm to 400 µm	Representative water sample. Counts particles in liquid. Water must have sufficient TDS to be electrically conductive.	Particle size distribution or total number greater than a manually set threshold.	Portable. Requires AC power.	
Spectrex Particle Counter	1 µm to 100 µm	Representative water sample. Counts particles in liquid.	Total number of particles greater than a manually set threshold.	Portable. Requires AC power.	
HIAC and Royco Counters	2 µm to 900 µm	Flowing water sample piped through flow cell or batch sample.	Particle size distribution	Portable. Most require AC power. Some battery powered units available.	

Figure 2.8 Suspended Solids Filtered from
Aegean Seawater
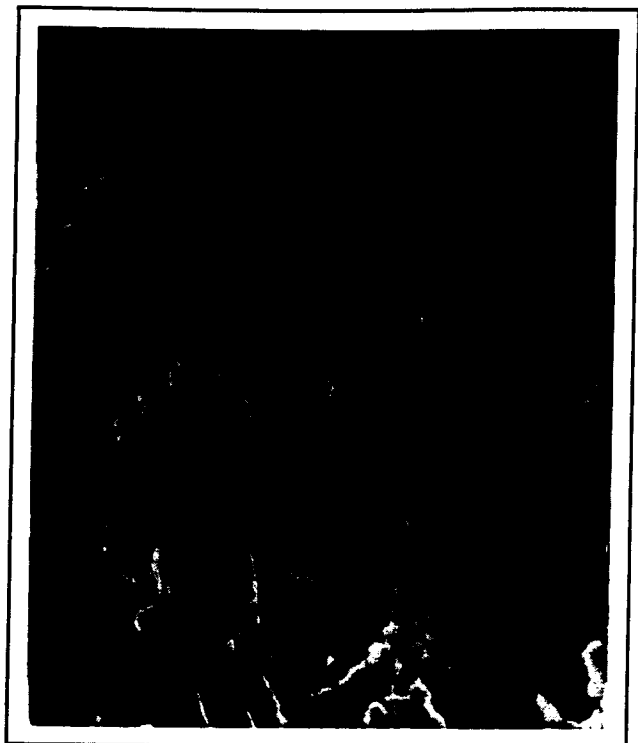Magnification = 1000 x
(Courtesy Brown & Root, Inc.)

Figure 2.9 Suspended Solids Filtered from
North Sea Water
Magnification = 1000x
(Courtesy Nalfloc Ltd.)

A fixed volume of water containing suspended particles is forced through the orifice. As each particle passes through the orifice, the increased resistance results in a voltage pulse which is proportional to particle volume. The series of pulses produced by a series of particles passing through the orifice are electronically scaled and counted, yielding a particle size distribution.
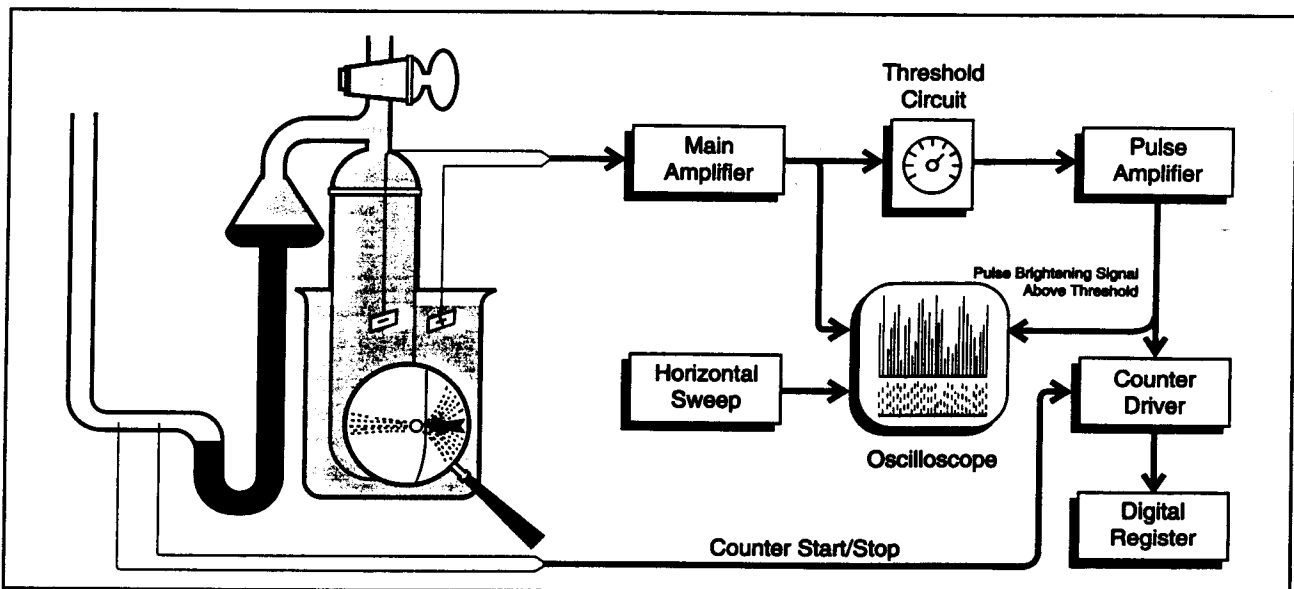
Figure 2.10 Coulter Counter Schematic *(Courtesy Coulter Electronics Ltd.)*

It must be realized that the particle "diameter" given by the counter is the diameter of a fictitious sphere with the same *volume* as the real particle. Thus, the more non-spherical the particle, the greater the error.

It should be noted that the Coulter Counter cannot distinguish between solid particles, oil droplets and gas bubbles. Therefore, water must be degassed prior to analysis and accurate particle counts cannot be obtained in waters containing oil droplets.

Light Scattering Counters

Instruments such as those manufactured by HIAC (HIAC Instruments Div., Pacific Scientific Co., Montclair, California) and Royco (Royco Instruments, Inc., Menlo Park, California) use the principle of light absorption/total scatter, or light blockage, to detect particles in a fluid. Water is flowed through a sensor cell and as each particle passes through the intense beam of light in the sensor, it scatters the light. The instrument measures the magnitude of each pulse of scattered light which is proportional to the *surface area* of the particle. The particle diameter given by the instrument is the diameter of a sphere with the same surface area as the particle.

The Spectrex Laser Particle Counter (Spectrex Corp., Redwood City, California) operates on the same principle, but uses a laser as a light source. Furthermore, in this instrument, the water sample remains stationary while the laser scans the sample. A sample container of water is placed in the instrument and the laser is activated. The beam revolves rapidly as shown in Figure 2.11, thus scanning a fixed volume of the sample. It gives a count of the total number of particles per milliliter above a certain manually set threshold between 1 μm and 100 μm.
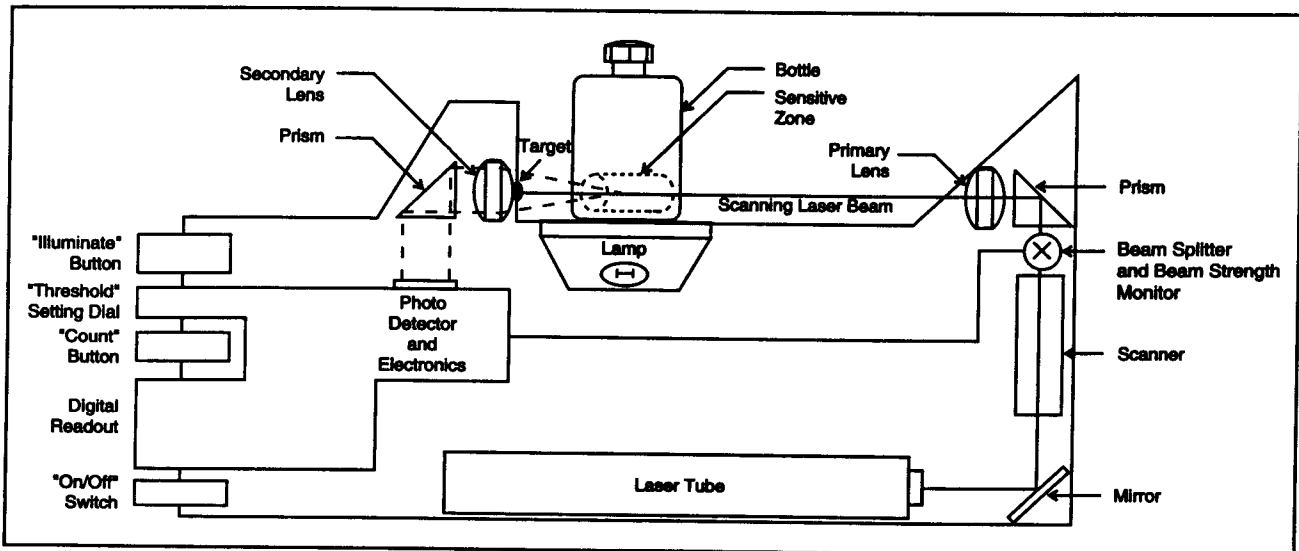

Figure 2.11 Spectrex Particle Counter *(Courtesy Spectrex)*

As in the case of the Coulter Counter, light-scattering particle counters cannot distinguish between solid particles, oil droplets and gas bubbles. Therefore, water must be degassed prior to analysis and accurate particle counts cannot be obtained in waters containing oil droplets.

Membrane Filter Analysis

Membrane filters *should not be used* to estimate the size of suspended solid particles in water, as the results have little meaning.

Two techniques are used.

1. Filter a water through two membrane filters in series, the second filter having a smaller pore size than the first, and measure the amount of suspended solids on each filter. The assumption is that the results can be used to estimate the concentration of particles in different size ranges.

    For example, filter one liter of water through a 5 μm pore-size filter followed by a 2 μm pore-size filter as shown in Figure 2.12. Determine the weight of suspended solids on each filter.
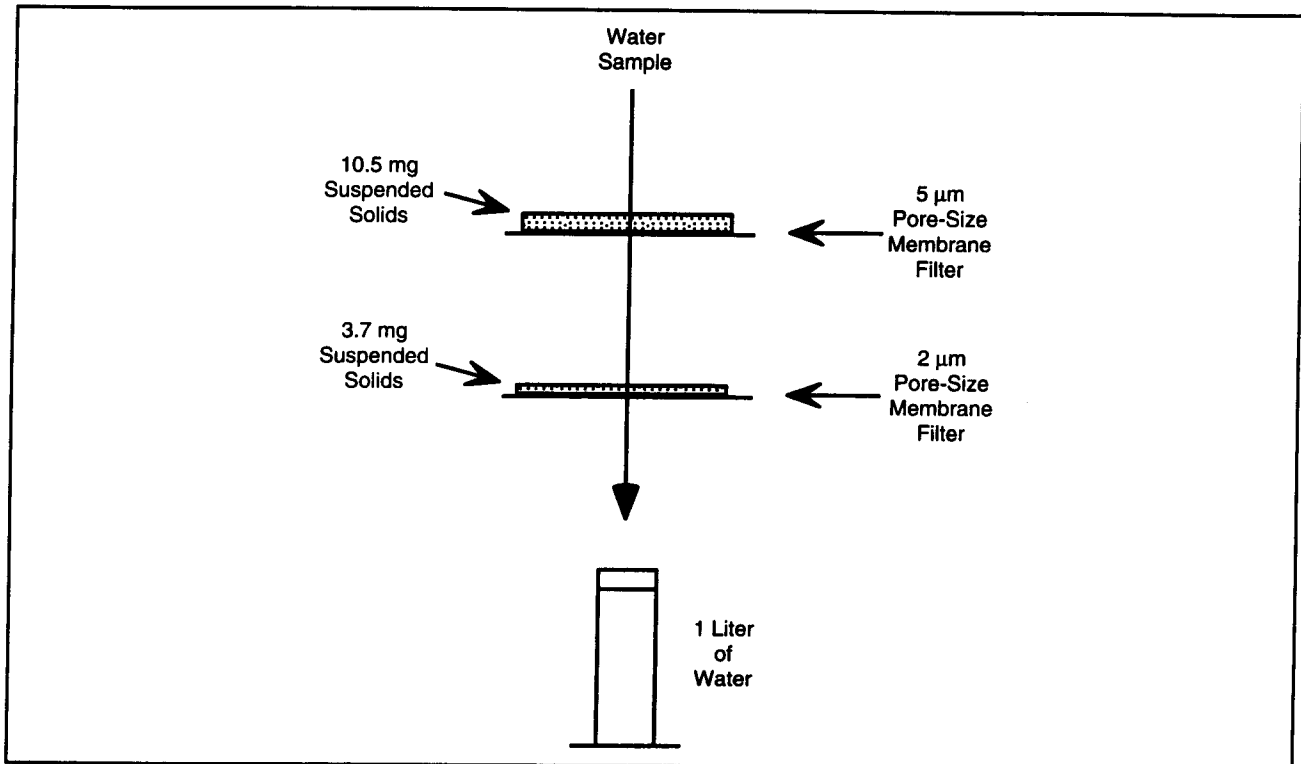

Figure 2.12 Filtration Through Membrane Filters in Series to Determine Particle Sizes

The results are erroneously interpreted as follows:

Particle Diameter	Concentration
$D \geq 5\mu m$	10.5 mg/L
$5\mu m > D > 2\mu m$	3.7 mg/L

This concept is analogous to a sieve analysis for sizing dry particles. However, the set of sieves is shaken vigorously throughout the sieving operation which prevents bridging and gives each particle in the sample the opportunity to pass through a given mesh-size.

Particle bridging occurs when particles are filtered from a liquid slurry which often results in the removal of particles smaller than the membrane pore size. The filter cake formed on the membrane becomes the filter.

2. The second technique employed is to filter a given water through a membrane of a given pore size. Then a second sample is filtered through a different pore size. Consider the example shown in Figure 2.13.
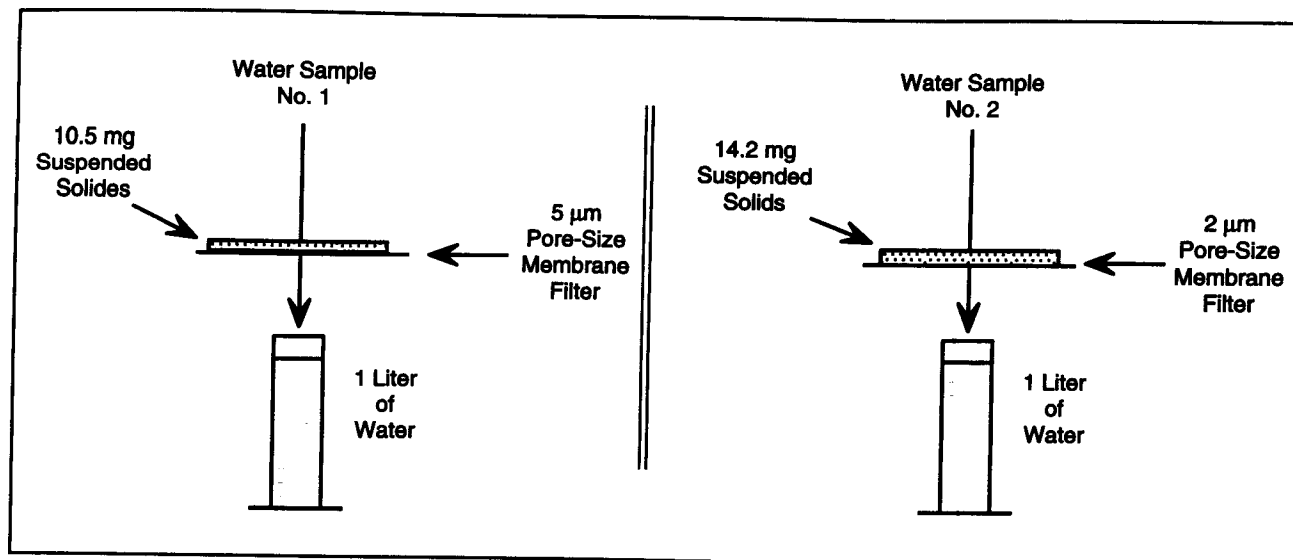

Figure 2.13   Filtration Through Membrane Filters in Parallel to Determine Particle Sizes

The results are erroneously interpreted as follows:

Particle Diameter	Concentration
$D \geq 5\mu m$	10.5 mg/L
$5\mu m > D > 2\mu m$	$14.2 - 10.5 = 3.7$ mg/L

Once again, the assumption is made that all particles with diameters less than the pore-size of the membrane filter being used will pass through the filter. However, this is not true because of particle bridging.

Filtration of particles from a liquid slurry is a process which is distinctly different from a sieve analysis of dry particles and *should never be used* to estimate particle sizes.

Turbidity

Turbidity is an optical property of a liquid which is related to the ability of undissolved particles to scatter light.

In most cases we are interested in a correlation between turbidity and suspended solids content. Unfortunately, *no general correlation is possible* because turbidity values are dependent upon the size, color, shape and refractive index of the particles, as well as the refractive index of the carrier medium. It is also dependent upon the wavelength of the incident light and the orientation of the scattered light detector, which means that different types of instruments can give different readings. A correlation between turbidity and suspended solids concentration can be made for a specific water containing a given quantity and size distribution of suspended particles. However, since turbidity values are a function of particle size, a change in particle size distribution will alter the measured turbidity.

Figure 2.14 illustrates the relationship between particle size and the amount of scattered light for a constant weight concentration of suspended particles. The optical response may be divided into three zones:
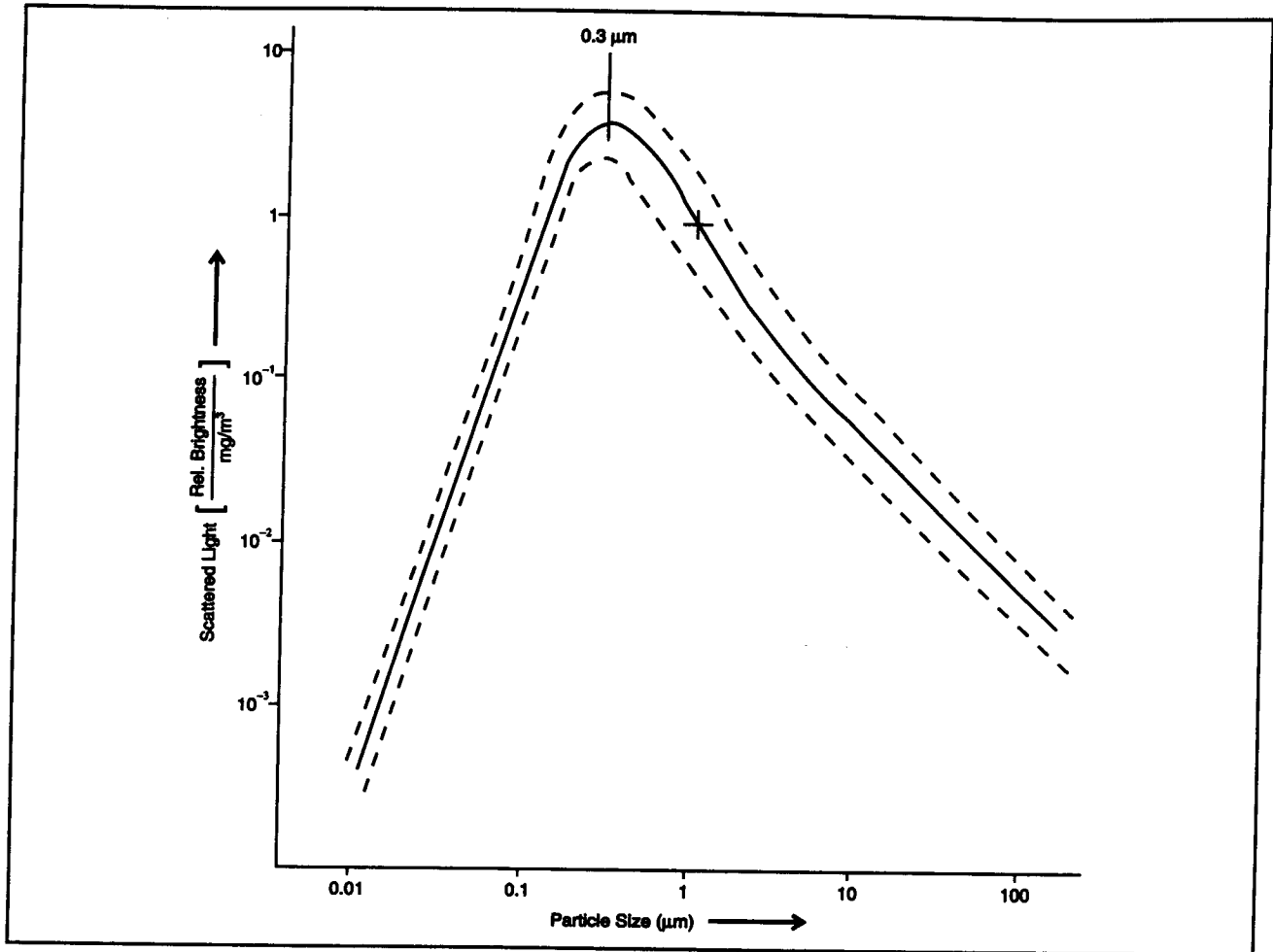

Figure 2.14 Scattered Light as a Function of Particle Size *(Courtesy Sigrist-Photometer AG)*

TABLE 2.15

Scattered Light vs Particle Size

Particle Size	Amount of Scattered Light
<0.1μm	Increases with particle size
0.1μm-1.0μm	Complex transition zone
>1.0μm	Proportional to total surface area. Decreases with particle size

Remember that these relationships apply when the concentration of suspended solids remains constant and only particle size changes. Above 1.0 μm, for example, the amount of light scattered is greater for a larger particle because it is proportional to surface area. However, as particle size increases, it takes fewer particles to give the same weight of suspended solids. The net result is a decrease in the total amount of light scattered.

When a ray of light hits a particle it is scattered in all directions. However, it is not scattered uniformly in all directions, with the result that the scattered light reading obtained for a given particle will be a function of the position of the detector.

For particles less than 0.1 μm diameter, the forward and backscattered intensities are equal, with half that intensity in the perpendicular direction (side scatter) as shown in Figure 2.15.
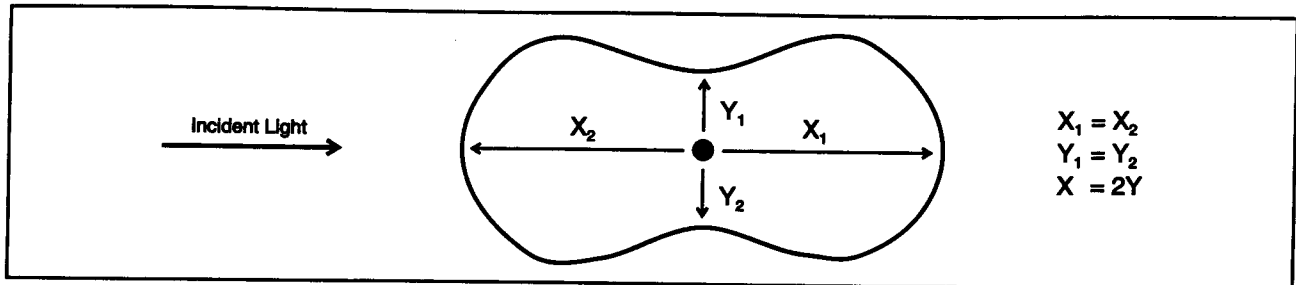

Figure 2.15   Angular Distribution of Scatter Light (Particle Diameter <0.1μm)

The pattern is not affected by particle shape as long as no dimension of the particle is greater than 0.1 μm.

For particles larger than 0.1 μm, the amount of forward scatter increases relative to the amount of back and side-scatter (Figure 2.16).
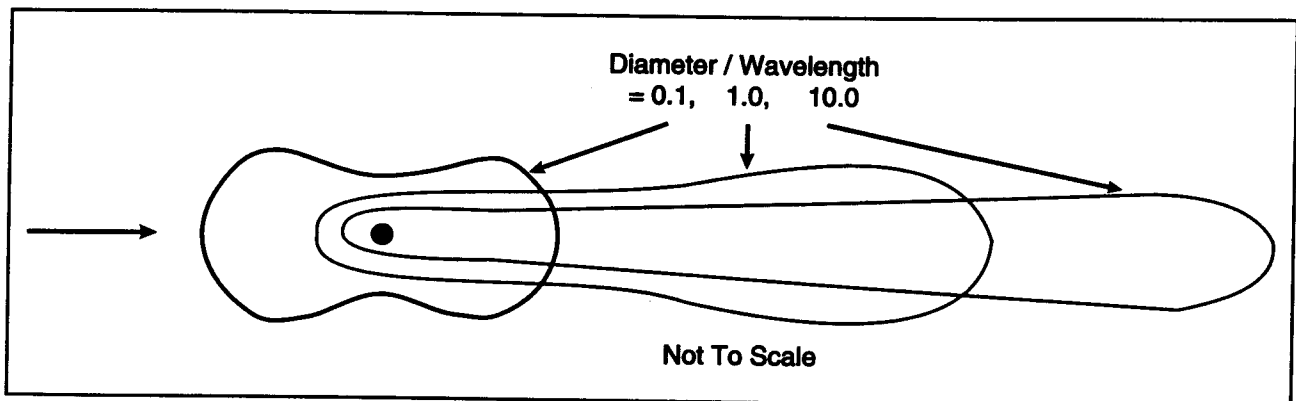

Figure 2.16   Angular Distribution of Scattered Light for Different Particle Diameters
(Courtesy Monitor Technology, Inc.)

The shape and orientation of non-spherical particles will modify the pattern, but in practical situations, the random orientation of the particles will generate essentially the same results as spherical particles of the same average volume.

There are many turbidity instruments on the market. The majority used in water injection systems either measure side scatter or forward scatter. An instrument which measures side scattered light at an angle of 90° to the incident light is called a nephelometer. Forward scatter instruments usually measure the scattered light at an angle of 15-30° to the incident light beam.

Selection of an instrument for a particular water should be based on a knowledge of the nature and size distribution of the suspended particles, and a careful investigation of the response characteristics of each instrument being considered.

The units in which turbidity measurements are reported can be extremely confusing.
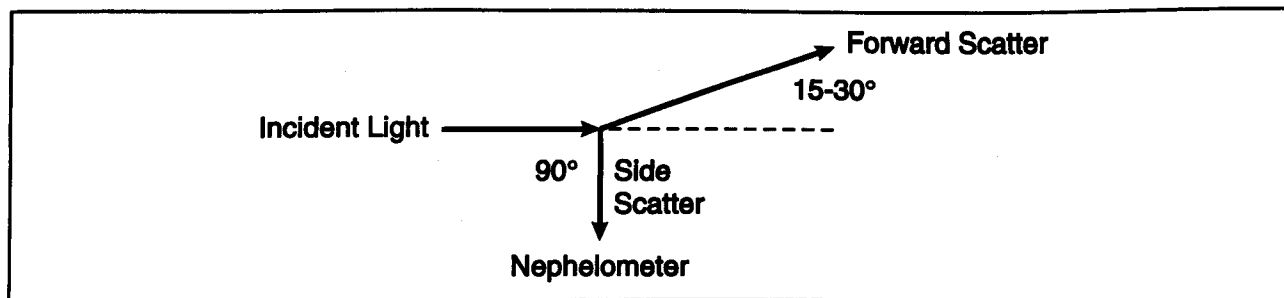
Figure 2.17 Scattered Light Direction

The father of modern turbidimeters is the Jackson Candle Turbidimeter. It consists of a vertical glass tube, graduated in units of length, and a candle as shown in Figure 2.18.

A sample of liquid is poured into the tube until the candle can no longer be clearly seen. The height of liquid at which this occurs is dependent upon its turbidity. A standard table is used to convert this height into Jackson Candle Units (JCU's), also called Jackson Turbidity Units (JTU's). With the advent of modern turbidimeters, other units began to appear. These units are based on calibrations made with standard suspensions of materials such as kieselguhr (diatomaceous earth or SiO_2), fullers earth, or formazin (a polymer suspension). Of the many units in use, the following are the most common:
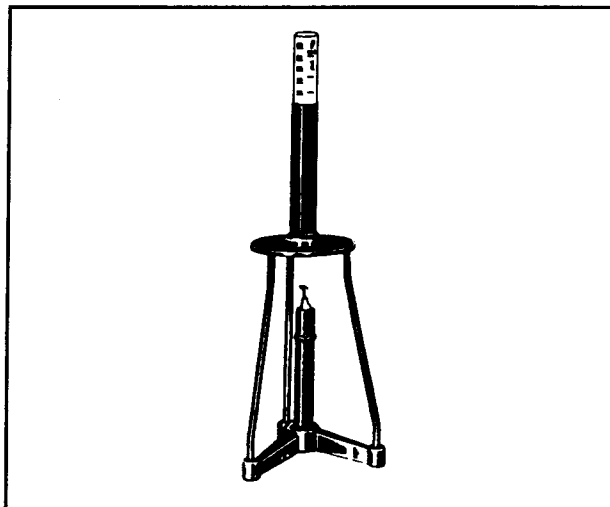

Figure 2.18 Jackson Candle Turbidimeter

- FTU — Formazin turbidity unit. An instrument is calibrated in FTU's with a standard suspension of formazin. Unfortunately, at least three different "standard" suspensions are used, resulting in three different formazin units.
- NTU — Nephelometer turbidity units are used solely for nephelometers. Nephelometers can be calibrated with kieselguhr, fullers earth or formazin.
- PPM — Parts per million. Actually ppm of the calibration suspension, which usually is diatomaceous earth (SiO_2) or fullers earth. It's use was originally intended to detect breakthrough of DE particles downstream of DE filters. It is not the concentration of the suspended solids in the water.

To make matters more confusing, readings taken with a particular instrument in a given water may not agree with readings taken with another type of instrument in the same water, even when the same turbidity units are being used. This can result from differences in calibration techniques, instrument design or the angle at which the scattered light sensor is located. Conversion among different unit systems must be made with extreme caution.

In summary, turbidimeters are extremely valuable instruments for monitoring suspended solids levels in water systems. However, a separate correlation between suspended solids concentration and turbidity values must be made for each water using a specific turbidity measuring instrument.

Field Water Analyses

As previously stated, certain water properties change very quickly after sampling. The determinations listed in Table 2.16 must be made on-site for maximum accuracy:

- The suspended solids should be collected in the field with a membrane filter by allowing a stream of water to flow through the filter. The filter paper and the collected solids are normally taken to a laboratory for analysis.

- Particle size distribution carried out with either a Coulter Counter or a light scattering device must be performed on a fresh sample to minimize the effect of precipitation of solids after sampling.

- The culture media should be inoculated in the field immediately after sampling, if possible. (See Chapter 5)

TABLE 2.16
On-Site Measurements

Parameters to be Measured On-Site	
pH	Temperature
Carbonate Ion	Suspended Solids Concentration[2.1]
Bicarbonate Ion	Particle Size Distribution[2.2]
Dissolved Oxygen	Turbidity
Dissolved Carbon Dioxide	Water Quality
Total Sulfides as H$_2$S	Bacteria Counts[2.3]

It is difficult to overemphasize the importance of field analyses. Certain properties may begin to change within minutes; others will be stable for several hours; and some are stable indefinitely.

For example, the pH and dissolved gas content of produced water will usually begin to rise immediately after the sample is taken. This results from the fact that dissolved acid gases begin to escape from solution as soon as the sample is removed from the system due to the reduction in pressure.

The rise in pH along with an increase in temperature may result in the formation of calcium carbonate scale. Bacteria in the sample may begin to multiply within a few hours — or they may begin to die — depending on specific conditions. Little or no H$_2$S or CO$_2$ may be found in the sample after a short time period.

If the sample contains dissolved iron, exposure to atmospheric oxygen will result in the precipitation of the iron due to reaction with oxygen.

$$4Fe^{++} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8H^+$$
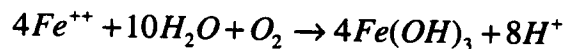
The generation of hydrogen ions will cause the pH of the sample to drop and lead to an error in the measured value. This is yet another reason why the pH should be measured on-site in a flowing sample.

Thus, if the sample were transported to a laboratory and analyzed after several days, the resulting analyses would give a very distorted picture of the water as it actually existed in the system, because of the changes in water composition which took place after the sample was removed from the system.

Had it been a sample of fresh surface water or a sample of seawater, different changes would be anticipated. However, regardless of the water source, field analyses are absolutely necessary for an accurate and meaningful assessment of oilfield water problems.

Field water analysis kits are available from several manufacturers, as are oxygen analysis equipment, pH meters, and membrane filter equipment. This equipment, and someone skilled in its use, is required during initial sampling, for monitoring of system performance, and for trouble shooting. If you or someone in your organization do not have field analysis skills, then reliable outside personnel should be retained to do the work for you. The important point is that on-site measurement of certain water properties is an integral part of the successful design and operation of a water injection system. Make certain that this point is not overlooked, and that the measurements are carried out by experienced personnel.

General Instructions for Making Analytical Determinations in the Field

Cleanliness

The axiom that "cleanliness is next to Godliness" is the first rule of life to an analytical chemist. Although we may occasionally get a bit sloppy in performing analyses in the field, it is important that we follow this rule as closely as possible in our own analytical work.

The laboratory analyst uses glass beakers, flasks and burettes which he carefully washes and cleans between each usage. This mode of operation is very unhandy in the field. Experience has shown that the use of plastic beakers (disposable), disposable plastic or glass syringes, plastic bottles (disposable) and glass bottles where necessary (disposable) is much easier. Our motto is "Never use anything twice." Throw it away rather than risk contaminating the sample.

The reasoning behind this preoccupation with cleanliness is extremely sound. If you go to a great deal of time and trouble to obtain an uncontaminated, representative water sample and then use a dirty beaker or burette to run your analysis, you have just wasted a lot of time. Your sample is contaminated by any material which may have remained in the analytical ware from the previous analysis. It may or may not have ruined your present analysis, but the chances are good that it has. There are many sources of uncertainty under the best of circumstances. Do not use dirty lab ware and avoid at least one of the known sources of error.

It is permissible to re-use some of the disposable beakers or syringes when analyzing a given water sample. Between determinations they should be carefully rinsed with de-ionized water or preferably with some of the water sample of interest. They must be thrown away after completing the analysis of the sample.

Some discretion is required in the question of cleanliness. If you want to take the time and trouble to clean up your plastic beakers and syringes between determinations, you can do so, just as is done with glassware in a laboratory. However, it is simply often very inconvenient or impossible to do so in the field. The use of inexpensive, disposable materials gives you the alternative of starting with new, clean materials each time. This procedure offers the dual advantage of saving you time and trouble, and of minimizing the possibility of contamination.

Use of Syringes

Syringes are very handy for measuring water sample volumes in the field instead of burettes. A sample volume of 10 mL or 25 mL is most common.

Syringes can also be used for titrating instead of a burette. One-mL and 5-mL syringes are most common for this purpose.

You should always use at least one-half of the volume of any syringe, whether you are measuring a sample or titrating. With less than half of a syringe volume, you lose accuracy. Use a smaller syringe instead.

Normally, when measuring a water sample volume, a needle is not used with the syringe. Titrations are made with syringes equipped with needles so that the titrant may be dispensed drop-by-drop. The use of syringes is detailed in Appendix 10.

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