

Water Quality

Not all impurities water encounters during the hydrologic or water cycle present a problem (see Water Basics). The water user's particular needs and requirements must be taken into consideration first. For example, some minerals give drinking water "taste" and may therefore be beneficial. Before one can assess the level of contamination, water quality criteria must be developed so that the appropriate tests may be performed to measure and identify specific contaminants or desirable ingredients.

Qualitative identification usually describes obvious physical conditions in water. These include color, odor, taste and clarity (turbidity). Quantitative water analysis is more precise than qualitative analysis. The tests follow more conventional methods of laboratory investigation and should be familiar. Following are the major quantitative analyses associated with water treatment.

Many individual impurities can be quantified through water analysis techniques. Below is a discussion of the most common individual contaminants.

Common Ions

It is a simple task to measure the type and concentration of dissolved minerals in water. A number of terms are used to express the level of mineral contamination in a water supply.

-Table 3 - Terms to Express Mineral Contamination

Term	Abbrev.	<u>Describes</u>
milligrams per liter	mg/L	(weight per volume)
parts per million	ppm	(weight in weight)
parts per billion	ppb	(weight in weight)
parts per trillion	PpT	(weight in weight)
grains per gallon	gpg	(weight per volume)
milli-equivalents per liter	m eq/L	(weight per volume)

A conversion table (Table 4) illustrates the relationships.

Water begins to transform to hard water when calcium - and/or magnesium-bearing minerals are dissolved by groundwater.

"Carbonate" and "non-carbonate" hardness are terms used to describe the source of calcium and magnesium. "Carbonate" hardness results from dolomite limestone (calcium and magnesium carbonate) while "non-carbonate" hardness comes from chlorine (chloride) and sulfur (sulfate) salts. The problems created by water hardness are numerous. Even levels as low as 4.5 to 7.5 mg/L (0.45 to 0.55 gpg) are too excessive for many common industrial applications.

As we have discussed, the presence of calcium (Ca-) and magnesium (Mg++) in a water supply is commonly known as "Water Hardness". It is usually expressed in grains per gallon (gpg). Hardness minerals exist in virtually every water supply, though at varying levels. The following table classifies the degree of hardness.

• Table 5 - Water Hardness Classification

<u>Hardness Level</u>		<u>Classification</u>
<u>mg/L</u>	<u>gpg</u>	
0-17	<1	soft water
17-60	1-3.5	slightly hard water
60-120	3.5-7.0	moderately hard water
120-180	7.0-10.5	hard water
>180	>10.5	very hard water

The problems created by hardness are numerous. Even levels as low as 5 to 8 mg/L (0.3 to 0.5 gpg) are too extreme for many uses.

Iron is a common water contaminant, since it makes up 5% of the earth's outer layer or crust. Iron is also one of the most difficult contaminants to remove because it may change electron valence states - that is, change from the water-soluble ferrous state (Fe+2) to the insoluble ferric state (Fe+3). In solution, ferrous iron behaves like calcium and magnesium or hardness. However, when oxygen or another oxidizing enabling agent is introduced, ferrous iron becomes ferric which is insoluble and precipitates, leading to a rusty (red brown) appearance in water. This change can occur when deep well water is pumped into a distribution system and oxygen is introduced into the water. Ferric iron can create havoc with pumps, valves, plumbing, water

treatment equipment (e.g. DI), and water-using devices (e.g. chillers).

Although **Manganese** (Mn^{+2}) behaves similarly to iron, lower concentrations of manganese can cause water system problems. But because manganese is encountered less frequently than iron, it is a smaller problem overall. Manganese forms a dark gray, almost black, precipitate.

Sulfates (SO_4^{-2}) are very common. When present at low levels, they may create problems in critical manufacturing processes. At high levels, sulfates are associated with a bitter taste and laxative effect. Many divalent metal-sulfate salts are virtually insoluble and precipitate out at relatively low concentrations.

Chlorides (Cl^{-}) are a common water contaminant. The critical level of chlorides depends on the intended use of the water. At high levels, they cause a salty or brackish taste, and may interfere with some water treatment methods. Chlorides will corrode exposed metal of water supply systems, including copper and some types of stainless steels.

Alkalinity is a generic term used to describe carbonates (CO_3^{-2}), bicarbonates (HCO_3^{-}) and hydroxides (OH^{-}). When present along with water hardness and certain heavy metals, alkalinity will contribute to scaling. The presence of alkalinity may be detected by an increase in pH.

While **Nitrates** (NO_3^{-}) and **Nitrites** (NO_2^{-}) may occur naturally, their presence in a water supply usually indicates human generated contamination or pollution. The most common sources of nitrate/nitrite contamination are primary or secondary sewage, industrial chemicals, fertilizers and animal wastes. Excessively high nitrate levels are toxic to humans, especially young children, and contribute to the loss of young livestock on farms with nitrate-contaminated water supplies.

Chlorine, because of its disinfectant qualities, is involved in treatment of most municipal water supplies. It is usually monitored as free chlorine (Cl_2) in concentrations of 0.1 to 2.0 PPM. In solution, chlorine gas dissolves and reacts with water to form the hypochlorite anion (ClO^{-}) and hypochlorous acid ($HClO$). The relative concentration of each ion is dependent upon pH. At a neutral pH of 7, essentially all chlorine exists as the hypochlorite anion, which is the stronger oxidizing form. Below a pH of 7, hypochlorous acid is dominant, which has better disinfectant properties than the anion counterpart.

In some instances, chlorine may be present as **Chloramine** (i.e. monochloramine, NH_2Cl) as a result of free chlorine reacting with ammonia compounds. The ammonia is added to a water supply to "stabilize" the free chlorine. Although chlorine's anti-microbial action is generally required, chlorine may also create disagreeable odor and taste. It also forms small amounts of tri-halo methane compounds (THM's), which are an increasing health hazard concern as a suspected precursor to carcinogenic materials.

Chlorine Dioxide (ClO_2) is generally produced on-site primarily by large municipalities. A reaction between chlorine or sodium hypochlorite and sodium chlorite is the typical method of chlorine dioxide generation. A more costly source of chlorine dioxide is available as a stabilized sodium chlorite solution.

Chlorine dioxide has been used for taste and odor control and as an efficient biocide. Chlorine dioxide can maintain a residual for extended periods of time in a distribution system and does not form tri-halo methanes (THM's) or chloramines if the stabilized chlorine-free form of generation is used. The possible toxicity of the chlorate and chlorite ions as reaction by-products may be concern for certain critical use water applications.

Silicon dioxide or silica (SiO_2) occurs naturally at levels ranging from a few PPM to more than 200 PPM. It is second only to carbon as the most prevalent element in the world. Therefore almost every water supply contains at least some silica. The problems created by silicon dioxide are associated with scaling or "glassing" in boilers, stills, and cooling water systems, or deposits on turbine blades.

An unusual characteristic of silicon dioxide is its solubility. Unlike most ions, silica is less soluble at higher temperatures. Silica is usually encountered in two forms: ionic (reactive) and colloidal (non-reactive).

Ionic or reactive silica exists as one of the several complexes silicon dioxide can form. It is not highly ionic and therefore is not easily removed by ion exchange. However, when concentrated to levels above 100 PPM, it polymerizes and may form a colloid. As such, it can vaporize in a boiler and carry over with the steam.

At concentrations over 100 PPM, silicon dioxide forms colloids of 20,000 molecular weight to 2 microns. It is difficult to remove by a particle filter, as it tends to form a gel. Colloidal silica is

easily removed with ultra-filtration or can be reduced by chemical treatment (lime).

Silica can lower the efficiency of filtration systems (such as reverse osmosis) when in excessive quantities. In low concentrations, it can affect yields in semiconductor manufacturing and is a major concern in high-pressure boiler systems. Once formed, silica scale is extremely difficult to remove.

Aluminum (Al^{+3}) may be present as a result of the addition of aluminum sulfate ($Al_2(SO_4)_3$) known as alum, as a flocculent. Aluminum can cause scaling in cooling and boiler systems, is a problem for dialysis patients, and may have some negative effects on general human health.

The **Sodium** ion (Na^+) is naturally introduced due to the dissolution of salts such as sodium chloride ($NaCl$), sodium carbonate (Na_2CO_3), sodium nitrate (Na_2NO_3) and sodium sulfate (Na_2SO_4). It is commonly added to water during the exchange of minerals in water softening or ion discharge from industrial brine processes. By itself the sodium ion is rarely a problem, but when combined with chlorides (Cl^-) or hydroxides (OH^-), it can cause corrosion of boilers, and at high concentrations (such as seawater), it will corrode some types of stainless steel.

Potassium chloride (KCl) is similar but less common than sodium chloride. It is used in some industrial processes. KCl is a problem only when ultrapure water quality is required.

Most **Phosphates** commonly enter surface water supplies through run-off of fertilizers and detergents where it is a common ingredient. They also enter through the breakdown of organic debris. Phosphates are used as an anti-scalant in boiler systems. At normal levels they do not cause a problem, unless ultra-pure water is required.

Dissolved Gasses

Dissolved **Carbon Dioxide** (CO_2) forms carbonic acid (H_2CO_3), reducing the pH and contributing to corrosion in water lines, especially steam and condensate lines.

Hydrogen Sulfide (H_2S), infamous for "rotten egg" smell, can contribute to corrosion. **Dissolved Oxygen** (O_2) can corrode water lines, boilers, and heat exchangers, but is only soluble to 13 PPM.

Radon is a water-soluble gas produced by the decay of radium. The predominant form in water supplies is Rn. It is naturally found in groundwater from granite formations, phosphate deposits and uranium deposits. Radon may cause human health problems, including cancer.

Heavy metals, such as lead, arsenic, cadmium, selenium, and chromium have harmful human health effects when present above certain levels. In addition, small concentrations may interfere with pharmaceutical products and medical procedures as well as laboratory and industrial processes of a sensitive nature.

Dissolved organic compounds are carbon-based materials and occur as the result of material decomposition or arise as man-made synthetic compounds. Tannin, humic and folic acids are common natural organic contaminants. They detract from the aesthetics of water but, unless they combine with certain halogens, they have no known negative health consequences. Under conditions of free halogen compounds chlorine or bromine, they form chlorinated hydrocarbons and tri-halo methanes (THM's) which are suspected carcinogens. Municipal water systems have maximum allowable limits of THM's set by the U.S. Environmental Protection Agency (EPA).

A variety of synthetic organic compounds with potential for negative health impact exist in many water systems from the proliferation of industrial and agricultural chemicals in the environment. Because these compounds are not easily biodegradable, they leach into soils or are carried into surface water features. Many of these compounds are suspected carcinogens.

Volatile Organic Compounds (VOC), such as carbon tetrachloride, chloroform, and methylene chloride, have relatively low molecular weight, and therefore easily volatilize into liquids or vapor. Most are introduced into the water supply in their liquid phase. When ingested, they may be absorbed into the bloodstream. Again, many are either known or suspected carcinogens.

Radioactive Substances

Water in itself is not radioactive, but may contain radionuclides, introduced either from naturally-occurring isotopes (very rare) or refined nuclear products from industrial or medical processes, radioactive fallout, or nuclear power plants. These obviously dangerous contaminants may be screened for using Geiger counters or other similar devices. In summary, water quality criteria must be determined before qualitative or quantitative testing can

commence. Contaminants must be defined and categorized first. Additional questions or considerations may arise by developing the water quality criteria. Is a peculiar taste the result of a presence of bacteria or is the real reason due to unusual levels of mineral? Is a turbid condition the result of inorganic silt or the presence of organic particles? Measurement of color units may describe the intensity of the color without but generating insight about the source or concentration.

Color

Color is determined mainly by organic material. Color indicates a given level of impurity, and while aesthetically unpleasing, it is generally not an indicator of health issues. Color may be measured by visual comparison of samples with calibrated standards or known concentrations of colored solutions.

Odor

Odor provides early indication of contamination which could be either hazardous or may affect the aesthetic quality of the water. The human nose is a very sensitive odor-detecting tool, as it can detect odors in low concentrations, down to the parts per billion (PPB) level. Odor therefore can be a useful qualitative measure of water quality.

Taste

Taste is a fairly accurate way to detect contaminant concentrations from a few to several hundred parts per million (PPM). However, it often cannot determine precise contaminants. A bad taste may be an indication of harmful contamination in drinking water.

Turbidity

Turbidity or clarity consists of inorganic and/or fine organic material suspended in water, causing a "muddy" appearance. Over a long period of time turbidity will settle by gravity due to small particle size. Turbidity is not a direct measurement of dissolved or suspended impurities. It's an indication of the degree of suspended matter present. Turbidity may be measured using the relative resistance of a solution to light. While it does not express an absolute level of contamination, it can be used qualitatively.

Particulates

Suspended matter can be expressed quantitatively in PPM or mg/L (milligrams per liter). This is accomplished by filtering the sample using a 0.45 μ (micron) disk, then drying and weighing the particles the filter traps. Silt Density Index (SDI) provides a relative value of suspended matter in water. The test consists of

the time required to filter 500 ml of a water sample through a 0.45µ filter. The SDI test is commonly used to measure the level of suspended solids (SS) in feed water to reverse osmosis (RO) systems.

pH

pH is a measure of hydrogen ion concentration in waters, specifically, the negative logarithm (log) of the hydrogen ion concentration. The relative acidic or basic level of a solution is measured by the pH scale of 0 to 14 (Illustration 2). A pH of 7.0 is called neutral, being neither acidic nor basic, with an equal number of hydroxyl (OH-) and hydrogen (H+) ions in concentration. A pH less than 7.0 denotes acidity while a pH more than 7.0 is considered alkaline or basic.

pH

0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
<-more acidic				neutral				more basic->						

Illustration 2 - pH Value

Logarithmic scales like pH and the Richter, which measures seismic activity, mean that each single unit value change in the scale represents a change in a multiple of 10 times the adjacent whole number value. For example, a pH of 8.0 is ten times more alkaline, and a pH of 9.0 is 100 times more basic than a pH of 7.0. Likewise solutions with a pH of 6.0 is ten times more acidic than 7.0 while a pH of 5.0 is 100 times more. The sharp sudden changes of a logarithmic scale can become problematic if not taken into consideration in the design of water treatment equipment and chemical selection. We can expect that pH values impact numerous water treatment applications, products and technologies.

Total Solids

Total Solids (TS) (Table 1) is the sum of Total Dissolved Solids (TDS) and Total Suspended Solids (TSS). In water analysis, these quantities are determined by obtaining and drying a sample then weighing the remaining solids. In the field, TDS is commonly measured by a conductivity meter (Illustration 3); however, this measurement is only an approximation, based on a calculation involving the conductivity and a constant. (See Table 2)

Table 1 - Total Solids (TS) = TDS + TSS

TDS		TSS	
<u>Organic</u>	<u>Inorganic</u>	<u>Organic</u>	<u>Inorganic</u>
Humic acid	Ions	Algae	Silt
Tannin	silica	fungi	rust
Pyrogens	(dissolved)	silica	floc
Bacteria		(colloidal)	



Illustration 3 - Portable TDS Meter

Ionic Contamination

Ions are electrically charged components (disassociated) of basic atomic particles. Being either negatively or positively charged

make them capable of conducting electricity. Theoretically pure water has few ions or charged particles, and so a high resistance to pass electrical current is experienced. Hence pure water is said to be "resistive" and is measured by units of electrical resistivity ($M\Omega$) and provides accurate representation of ionic concentration. Conductivity is described in units called microSiemens/cm ($\mu S/cm$) and is measured using a probe and conductivity meter (Illustration 4). Resistance being the inverse of conductivity, is measured with resistivity probes and meters (Illustration 5).



Illustration 4 - Portable Conductivity Meter



Illustration 5 - Field-Mount Resistivity Meter

Table 2 expresses the relative concentrations of sodium chloride versus conductivity and resistance. As a general rule dissolved ionic content, expressed in PPM, is approximately one-half to two-thirds that of the conductance of water.

Table 2 - Relative Concentration of Dissolved Minerals vs. Conductivity and Resistance

mg/L Sodium Chloride	Total Dissolved Solids mg/L CaCO ₃	Specific Conductance MicroSiemens/cm	Specific Resistance ohms'cm	Grains Per Gallon Sodium Chloride
0.05	0.043	0.105	9,523,800	0.0029
0.1	0.085	0.212	4,716,980	0.0060
0.2	0.170	0.424	3,558,490	0.012
0.3	0.255	0.637	1,569,850	0.018
0.4	0.340	0.848	1,179,240	0.023
0.5	0.425	1.06	943,396	0.029
0.6	0.510	1.273	785,545	0.035
0.7	0.595	1.985	673,400	0.041
0.8	0.680	1.696	589,622	0.047
0.9	0.765	1.908	524,109	0.053
1.0	0.85	2.12	471,698	0.06
2.0	1.70	6.37	156,985	0.18
4.0	3.40	8.48	117,924	0.23
5.0	4.25	10.6	94,339	0.29
6.0	5.10	12.73	78,554	0.35
7.0	5.95	14.85	67,340	0.41
8.0	6.80	16.96	58,962	0.47
9.0	7.65	19.08	52,410	0.53
10.0	8.5	21.2	47,169	0.58
20.0	17.0	42.4	23,584	1.17
30.0	25.5	63.7	15,698	1.75
40.0	34.0	84.8	11,792	2.34
50.0	42.5	106.0	9,433	2.92
60.0	51.0	127.3	7,855	3.51
70.0	59.5	148.5	6,734	4.09
80.0	68.0	169.6	5,896	4.68
90.0	76.5	190.8	5,241	5.26
100.0	85.0	212.0	4,716	5.85
200.0	170.0	410.0	2,439	11.70
300.0	255.0	610.0	1,639	17.5
400.0	340.0	812.0	1,231	23.4
500.0	425.0	1,008.0	992	29.2
600.0	510.0	1,206.0	829	35.1
700.0	595.0	1,410.0	709	40.9
800.0	680.0	1,605.0	623	46.8
900.0	765.0	1,806.0	553	52.6
1,000.0	850.0	2,000.0	500	585.5
2,000.0	1,700.0	3,830.0	261	117.0
3,000.0	2,550.0	5,670.0	176	175.0
4,000.0	3,400.0	7,500.0	133	234.0
5,000.0	4,250.0	9,240.0	108	292.0
6,000.0	5,100.0	10,950.0	91	351.0
7,000.0	5,950.0	12,650.0	79	409.0
8,000.0	6,800.0	14,340.0	69	468.0
9,000.0	7,650.0	16,000.0	62	526.0
10,000.0	8,500.0	17,600.0	56	585.0

Microbiological Contamination

Microbial concerns may be classified into viable and non-viable categories. Viables include organisms that proliferate under favorable conditions, such as bacteria (see **Bacteria**). Non-viables arise from the breakdown -or byproduct- of a viable organism.

Bacteria

Water is a necessary medium for bacterial colony health and reproduction because it transports nutrients and its temperature stability provides an environment conducive to growth. Water will support bacterial growth even with miniscule amounts of nutrients available. Therefore a constant challenge to water purity is natural contamination, bacterial growth and control.

Bacterial contamination is expressed as "total viable microbial counts per ml" or as "colony-forming units (CFU) per 100 ml." These are the most common in water treatment. CFU's are determined by culturing and incubating samples then counting the resultant growth with a Coulter Counter. The operating assumption being that each colony results from one bacterium.

Certain bacterial conditions can further complicate iron problems. Since bacterial organisms *Crenothrix*, *Gallionella* and *Sphaerotilus* use iron as an energy source, they eventually form a rusty, gelatinous sludge that fouls water conduits. When diagnosing iron problems, it critical to determine whether or not such iron-thriving bacteria are present.

Pyrogens

Pyrogens include any substance that can produce fever response in mammals. Pyrogens are commonly endogenous (from within the organism) but also may be exogenous (from without). Endotoxins are organic compounds that are shed during bacterial cell reproduction and growth and are chemically and physically stable. Endotoxins are not necessarily destroyed by conditions that normally kill bacteria. Pyrogen levels are quantified in Endotoxin Units (EU) per milliliter. Pyrogens are of significance to the pharmaceutical industry, since high concentrations may cause responses in humans ranging from fever, to shock, even death.

Testing for pyrogens was introduced during the 1940s using small rodents. These tests, while accurate identifiers of pyrogenic contamination, took too long and were expensive. Today the horseshoe crab or *Limulus* Amebocyte Lysate (LAL) test is commonly used. Endotoxins initiate clotting in the presence of an extract of the blood of the horseshoe crab, *Limulus polyphemus*. The LAL

test can detect pyrogens down to 0.03 EU/ml level. Newer automated kinetic turbidimetric methods can detect another order of magnitude lower to 0.001 EU/ml and are a simpler, cheaper test. Usually the LAL test is used only if there is a concern about endotoxins in the finished water, such as in pharmaceutical applications. However, due to the swift results of the LAL test (approx. 2 hours), other critical industries are beginning to use it as a quick indicator of possible bacterial contamination or Total Organic Carbon (TOC).

Total Organic Carbon (TOC) is a measure of organic material contamination in water, in mg/L units. TOC is a direct measure of the oxidizable organic material. OC is a very fine measurement used in sophisticated treatment systems - such as semiconductor grade water - where any micro contamination can adversely affect finished product quality.

Biochemical oxygen demand (BOD) is a measure of organic material contamination in water also specified in mg/L. BOD is the amount of dissolved oxygen required to meet the metabolic needs of aerobic microorganisms in water containing organic material. Typically, the test for BOD is conducted over an extended (10-day) period.

Chemical oxygen demand (COD) is another measure of organic material contamination in water specified in mg/L. **Chemical oxygen demand** is the amount of dissolved oxygen required to cause chemical oxidation of the organic material in water. Both BOD and COD are good indicators of the environmental health of a surface water supply. They are commonly used in wastewater treatment but rarely in general water treatment.