

ENVIRONMENTAL ANALYTES AND MATRICES

Physical Properties:	temperature, density colour, taste/odour, total solids turbidity (suspended solids) conductivity (dissolved solids) oxidation-reduction potential
Matrices:	rain water rivers/streams lakes/reservoirs groundwater oceans/marine sediments
Chemical Constituents:	inorganic ions (non-metals) metals organic molecules gases (oxygen and carbon dioxide)
Sampling Considerations:	representative sampling sampling container sample pre-treatment and preservatives quality control/quality assurance

Refer to:
Standard Methods for the Examination of Water and Wastewater
Canadian Water Quality Guidelines

Physical Properties of Water (refer to Standard Methods, section 200)

Inherent properties of water that do not rely on chemical reaction

- temperature, density
- colour, taste/odour
- turbidity, conductivity
- solids (dissolved and suspended)
- oxidation-reduction potential

Note: Standard Methods also include alkalinity and hardness as ‘physical properties’, however these are actually measures of chemical properties.

Hardness (Total vs Calcium) – measured volumetrically with EDTA buffered at pH ~ 10 (total) or pH ~ 12 (calcium).

Example: A sample has been analyzed by AAS to have $[\text{Ca}^{2+}] = 6.2 \text{ mM}$ and $[\text{Mg}^{2+}] = 0.50 \text{ mM}$. Express the total and calcium hardness as ppm CaCO_3 .

Alkalinity (Total vs Phenothalein)

A measure of acid neutralizing capacity, due to the presence of basic species present in water, e.g., HCO_3^- , CO_3^{2-} , OH^- , NH_3 , etc... In most natural waters the major contributor is bicarbonate, HCO_3^- .

Titration of sample to pH \sim 8.3 (phenolphthalein) or pH \sim 4.3 (methyl orange aka Total)

In units of mol/L of H^+ ; $[\text{alk}]_T$ & $[\text{alk}]_P$

In units of mg/L of CaCO_3 ; T_{alk} & P_{alk}

pH is NOT a good measure of alkalinity

Compare two solutions;

Solution 1: $[\text{OH}^-] = 1.0 \times 10^{-3} \text{ M NaOH}$; pH = 11.0 \therefore very basic

Solution 2: $[\text{HCO}_3^-] = 0.10 \text{ M NaHCO}_3$; pH = 8.34 \therefore less basic

Example: Consider a solution with a pH of 9.16, which has $P_{\text{alk}} = 12 \text{ mg/L CaCO}_3$ and a $T_{\text{alk}} = 200 \text{ mg/L CaCO}_3$. Determine the concentration of $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$ and $[\text{OH}^-]$.

COLOUR – due to the presence of a complex array of large organic molecules (humic and fulvic acids from the degradation of vegetative matter) complexed to certain metallic species particularly Fe^{3+} and Mn^{2+} .

True colour

Apparent colour

To assess true colour, must first remove suspended matter by filtration, co-agulation or centrifugation.

Colour reported in arbitrary ‘colour units’ based on a matching appearance to a dilution series of PtCl_6^{2-} and Co^{2+}

Calibration solutions made up in Nessler viewing tubes

Samples with colour > 70 CU, must be diluted prior to colour matching. Sample dilution then incorporated into reported value.

There are more complex spectrometric methods that give more details of specific wavelength absorptions.

Drinking water Guidelines:

World Health Organization (WHO) sets aesthetic limit of 15 CU

European Union (EU) has aesthetic limit of 20 CU

Most surface waters has colour $< 1 - 5$ CU

Colour may be due to natural and anthropogenic sources.

SOLIDS in a water sample can exist as either suspended (*filterable*) or dissolved (*non-filterable*).

Total Solids: The sum total of all solids both dissolved and suspended. Determined by evaporating a known sample volume to dryness at 105 °C. Some salts trap water molecules as hydrates, which will remain at this temperature. The mass of residue is expressed as mg/L or mg/kg.

Total Dissolved Solids (TDS): Those solids which are dissolved will pass through a 0.45 um filter; correlated to specific conductivity. Determined by filtering a known sample volume and evaporating the filtrate at a temperature of 180 °C. All water is driven off, some volatile organics may be lost and CO_2 is released from HCO_3^- salts. The mass of residue is expressed as mg/L or mg/kg.

Total Suspended Solids (TSS): Those solids which are not dissolved and will be trapped on a 0.45 um filter; correlated to turbidity. Determined by filtering a known sample volume through a pre-weighed filter media. The filter is dried at 105 °C and the mass of the residue is determined by difference. The mass of residue is expressed as mg/L or mg/kg.

Fixed Solids: Solids which do not decompose or evaporate at high temperature; correlated to inorganic mineral salts. Determined by heating the dried residue from either TDS or TSS to 550 °C in furnace. The mass of residual ash is expressed as mg/L or mg/kg.

Volatile Solids: Solids which decompose, evaporate or combust at high temperature; correlated to organic carbon. The mass of difference between of TDS or TSS residue before and after heating to 550 °C is expressed as mg/L or mg/kg.

Dissolved Organic Carbon (DOC) – Sample filtrate is evaporated and the residue is combusted at high temperature. The CO_2 produced is quantified and expressed as mg/L of carbon.

Particulate Organic Carbon (POC) – Filter residue is dried and combusted at high temperature. The CO_2 produced is quantified and expressed as mg/L of carbon.

TURBIDITY – a measure of light scatter due to the presence of suspended solids including fine silt, plankton, colloidal particles of inorganic minerals (e.g., Fe_2O_3 , MnO_2).

Secchi Disk

Jackson Tube

Nephelometer

High turbidity due to poor light penetration and high suspended particle loads.

Different instrument designs make it difficult to compare absolute readings.

Typical turbidity values:

Drinking water aesthetic limit < 5 NTU

However, most purveyors monitor closely and aim for < 1 NTU, due to cryptosporidium and other micro-organisms

Surface waters are 0 – 40 NTU's

During storms or freshet > 100 NTU's

CONDUCTIVITY – ability of a sample to allow the passage of an electrical current due to the presence of dissolved solids. It depends on the sum of the concentration of all ions, the temperature, the configuration of the conductivity cell (probe) and the inherent mobility of each ion (size, charge etc).

Units:

Conductivity Meters actually measure current necessary to hold a constant voltage across a conductivity cell. Platinized electrodes in the conductivity cell must be standardized by measuring conductivity of a solution of known conductivity to determine a cell constant.

Eg. 0.0100 M **KCl** solution has a specific conductivity = $1413 \mu\text{S cm}^{-1}$ at 25°C

Specific Conductivity of sample = Measured Conductivity (μS) x Cell Constant (cm^{-1})

Measurements must be temperature compensated (usually 2% per $^\circ\text{C}$)

Since conductivity is proportional to conc. of all ions, a high value is indicative of high Total Dissolved Solids (TDS) content. Therefore, conductivity is used as a surrogate for TDS. Conversion factors to convert $\mu\text{S cm}^{-1}$ to mg/L NaCl are specific to water source. Typically use $0.65 \text{ mg L}^{-1} \text{ NaCl}$ per $\mu\text{S cm}^{-1}$.

TDS meters are actually conductivity meters in disguise.

High conductivity can be indicative of

- coastal inflow in groundwater sources
- effluent contamination
- increased mineral leaching

Conductivity often used to monitor efficiencies of water treatment systems
Canadian Drinking Water Guidelines (CDWG) are aesthetic 500 mg/L NaCl

OXIDATION – REDUCTION POTENTIAL: a measure of the oxidizing ability of a sample. Affects the chemical speciation of many chemical constituents. Different ORP meters are constructed using different reference electrodes, therefore corrections may need to be incorporated to compare values to those recorded versus a Standard Hydrogen Electrode (SHE).

General ORP ranges:

ORP < -200 mV	anaerobic environment (reduced chemical forms present) (e.g., NH_3 , H_2S , CH_4 , Fe^{2+} , ...)
ORP > 0 mV	aerobic environment (oxidized chemical forms present) (e.g., NO_3^- , SO_4^{2-} , HCO_3^- , Fe^{3+} , ...)
ORP between -200 and 0 mV	transitional environment

COMPOSITION OF NATURAL WATERS

Natural waters contain dissolved and suspended materials that affect and are affected by water chemistry. The presence of these species is largely dependent on the source of the water.

1. Rain Water

Relatively low concentrations of specific dissolved solids. (generally < 5 ppm). Depends of air pollution and geography. For example, coastal rains often contain sea spray salts up to 15 ppm.

Typical rainfall:

Ion	SO_4^{2-}	Cl^-	NO_3^-	Na^+	K^+	Mg^{2+}	Ca^{2+}
Conc (ppm)	2	8	0.5	4	0.3	0.3	2
Conc (meq/L)	0.021	0.22	0.001	0.17	0.008	0.012	0.050

Relatively high concentrations of dissolved gases. (O_2 , CO_2 , SO_3 , NO_2 etc).

Gases may be natural (photosynthesis, volcanoes etc) or anthropogenic (industry, transportation etc).

Natural rainwater has pH ~ 5.6

Acid rain pH < 5

Other Gases:

2. Rivers and Streams

Composition depends on:

1. rain constituents
2. soil/mineral substrate
3. plant/animal life
4. human activity

major cations: Ca^{2+} , Mg^{2+} , Na^+ , K^+

major anions: $\text{HCO}_3^-/\text{CO}_3^{2-}$, SO_4^{2-} , Cl^- , NO_3^- , PO_4^{3-}

dissolved gases: $\text{O}_2(\text{aq})$
 $\text{CO}_2(\text{aq})/\text{H}_2\text{CO}_3$

dissolved organic matter: fulvic and humic acids

suspended solids:

human activity:

agriculture, logging, mining, pulp, food processing, urbanization

- fertilizers
- treated wastewater
- oils/hydrocarbons
- heavy metals

3. Lakes and Reservoirs

1. composition depends on:
2. inflow constituents
3. residence time
4. plant/animal activity
5. human activity

Lake stratification:

epilimnion

thermocline

hypolimnion

classification system

oligotrophic → mesotrophic → eutrophic

4. Groundwaters

composition depends largely on soil and rock type

- filtered through soil, sand and clay
- usually low in micro-organisms
- low oxygen content (ORP < -200 mV)

typically higher concentrations of Ca^{2+} , Mg^{2+} , HCO_3^-

Fe^{2+}

Mn^{2+}

Mineral Content in Hotsprings (ppm):

Ion	SO_4^{2-}	HCO_3^-	Na^+/K^+	Mg^{2+}	Ca^{2+}
Banff	572	138	5	36	205
Fairmount	1000	700	40	105	480

5. Marine and Ocean Waters

Concentration of all ions much higher than freshwater, but major ions in seawater are Na^+ and Cl^- rather than those in fresh surface water, which are Ca^{2+} and HCO_3^-

TDS ~ 35,000 ppm (i.e., 3.5 % or 35 ‰)

Na^+ ~ 12,000 ppm

Cl^- ~ 18,000 ppm

Note: Gas solubility is reduced in sea-water.

Therefore, DO meters and ISE's need to be specially calibrated to compensate for high ionic strength.