

MODULE 2.1**Analysis of major constituents in water**

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MODULE 2.1

Analysis of major constituents in water

In this section the analytical techniques which are used to determine major constituents in water both in the field and in the laboratory are described. After a brief introduction, the importance of correct sampling procedure is highlighted, followed by the brief outline of different methods that are commonly used for determination of various major constituents present in water.

Introduction:

It is needless to emphasise the importance of water in our life. We need water for different purposes; we need water for drinking, for industries, for irrigation, for swimming, for fishing etc.

Thus water for different purposes has its own requirements for the composition and purity and each body of water has to be analysed on a regular basis to confirm to suitability. The types of analysis could vary from simple field testing for a single analyte to laboratory based multi component instrumental analysis.

The analytical process involves sampling and sample storage since changes in composition of water do not stop once the sampling has been taken. Precaution has to be taken to make sure that the water reaching the laboratory has the same composition as it did when the sampling was done.

Water Sampling and Storage:

The representative sample of water that is taken should be the one that truly reflects the composition of the water sample to be analysed. Due to varying period of time that may lapse between sample collection and analysis, storage conditions must be such as to avoid undesirable losses, contamination or other changes that could affect the results of the analysis.

In some situations, a sampling plan or strategy may need to be devised so as to optimise the value of analytical information collected. For long term variation it may be beneficial to take samples at the same stage of each periodic cycle, whereas for short term variations such as seasonal, weekly or daily several samples have to be taken for each cycle.

For example oxygen is produced by photo synthesis in the day time but consumed by respiration or by oxidation of organic material continuously. A decrease in oxygen concentration during the night would be expected.

Variation of nitrate is more complex. It is a nutrient necessary for growth and if there were no additional inputs it would decrease in the spring growing season and increase in winter, but if a farmer puts an excessive amount of nitrate containing fertiliser on a neighbouring field, there would be a sudden increase in nitrate concentration in the river into which the field is drained.

The container materials to be used for sample collection may be made of glass or polythene. Trace metals may be depleted by adsorption if stored in glass containers, while sodium, potassium, boron and silicates can be leached from the glass into the sample solution. Plastic containers should always be used for such samples . Conversely sample solutions containing organic solvents and other

organic liquids should be stored in glass containers because organic compounds may be leached from the walls of the plastic containers. If volatile materials or dissolved gases are to be analysed, the container material must always be full. For other components, it is beneficial not to fill the container completely as the contents can then be more easily be mixed before analysis. Standard methods are available for most components to minimise the analyte for storage loss. The method of storage varies according to the physical and chemical properties of the species.

For example samples to be analysed for nitrate should be stored at 4°C to minimise the biological degradation; and samples to be analysed for pesticides should be stored in dark to avoid photochemical decomposition; and samples to be analysed for metal ions should be acidified to prevent adsorption of metal ions on the sides of the container; and samples to be analysed for phenols should be made alkaline with sodium hydroxide to lower the volatility.

Water Quality Measurement:

In this section, techniques which provide a measurement relating to the overall effect of groups of compounds or ions rather than measuring concentrations of individual components are described. Measurements that are discussed include **suspended solids, oxygen demand** (measuring oxidisable material), **total organic carbon, electrical conductivity and water hardness**.

Determination of suspended solids:

The main physical problem that may be caused by suspended solids in natural water bodies is that they cut down light transmission through the water and so lower the rate of photosynthesis in plants.

Also in less turbulent parts of the river some of the solids may sediment out, smothering the life on the river bed.

The suspended solid determination is extremely valuable in the analysis of polluted waters. It is one of the major parameters used to evaluate the strength of domestic waste waters and to determine the efficiency of treatment units. The analysis of the suspended solids is done by filtration and weighing once again. The suspended-solids determination is subject to considerable error if proper precautions are not taken. Usually the sample size is limited to 50 ml or less because of the difficulties encountered in filtration of larger samples. The weight of solids removed seldom exceed 20 mg and is often 10mg. Small errors in weighing or losses of filter mat can be quite significant. It is extremely important that the Gooch crucibles be carefully prepared and brought to constant weight before use. Sufficient sample should be filtered, if possible, to yield an increase in weight of about 10 mg.

Environmental significance of dissolved oxygen:

In liquid wastes, dissolved oxygen is the factor that determines whether the biological changes are brought about by aerobic or anaerobic organisms. The former use free oxygen for oxidation of organic and inorganic matter and produce innocuous end products, whereas the latter bring about such oxidations through reduction of certain inorganic salts such as sulphates, and the end products are often very obnoxious. Since both types of organisms are ubiquitous in nature, it is highly important that conditions favourable to the aerobic organisms (aerobic conditions) be maintained. Otherwise the anaerobic organisms will take over and the development of nuisance conditions will result. Thus dissolved-oxygen measurements are vital for maintaining aerobic conditions in natural waters that

receive pollutional matter and in aerobic treatment process intended to purify domestic and industrial waste waters.

The presence of oxygen in rivers is the result of photosynthesis by plants and by dissolution of oxygen from the atmosphere into the water. The solubility of oxygen in water is low. Water saturated with oxygen at 25°C contains 8.24mg l⁻¹. It would therefore be easy to deplete the oxygen content if any material were present which would react with oxygen. The material could be organic, as already discussed but could also be inorganic. For example iron in the form of Fe²⁺ can deplete oxygen by oxidation to Fe³⁺.

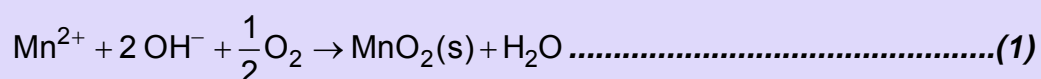
There are two distinctly different analyses which are useful to monitor environmental waters for oxygen. In the first analysis, the oxygen concentration in the sample (eg:river sample) is measured directly. This result would give an indication of the health of the river at a particular location and at the time of sampling. Since the oxygen level in a river can vary dramatically with location and with time, this result would be of less use for assessing the overall health of the river. In the second analysis, the amount of material known as oxygen demand which, given time, could deplete the oxygen in the river is measured. This oxygen demand gives an indication of possibility of oxygen depletion which will occur if the oxygen is not replenished. This measurement would be much more suitable for determining the overall health of the river since the oxygen demand of a water supply is unlikely to change suddenly.

The analytical methods used to measure oxygen demand also involves measurement of dissolved oxygen and hence measurement of dissolved oxygen will be discussed first.

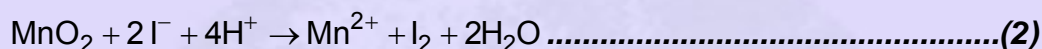
Measurement of dissolved oxygen:

The dissolved oxygen can be determined either by the Winkler (iodometric) method or by the use of dissolved oxygen electrodes. The results are either expressed as a simple concentration (mg l^{-1}) or as a percentage of full saturation. The concentration of oxygen in saturated water is dependent on temperature, pressure and salinity of the water and it is customary to think of dissolved oxygen levels of about 8mg l^{-1} as being the maximum available under critical conditions. Care must be exercised in the collection of samples to be used for dissolved oxygen determinations. All sampling devices are designed on the principle that contact with air cannot be avoided during the time the sample bottles are being filled. However, if the space is available to allow the bottles to overflow, a sample of water that is representative of the mixture being sampled can be obtained. Most samplers are designed to provide an overflow of two or three times the bottle volume to ensure the collection of representative sample. Most samples for dissolved oxygen are collected in the field and since oxygen values may change radically with time because of biological activity, it is customary to "fix" the samples immediately after collection. The usual procedure is to treat the samples with the conventional reagents used in dissolved-oxygen test and then perform the titration when the samples are brought to the laboratory.

In the Winkler's method the dissolved oxygen is reacted with Mn^{2+} immediately after sampling which is added in the form of manganese sulphate, together with an alkaline iodide/ azide mixture:



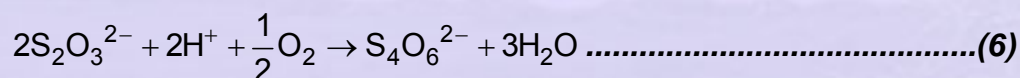
The iodide is necessary for the analytical procedure in the laboratory and the azide is present to prevent interference from any nitrite ions. Nitrite ions oxidise I^- to free I_2 under acidic conditions that can lead to erroneous results. Nitrite interference can be overcome by the use of sodium azide NaN_3 (eqns:3 &4). After transport to the laboratory, the sample is acidified which results in the reaction (2).



The released iodine can then be titrated with sodium using starch as indicator.



The overall reaction is



i.e: 4 mole of thio sulphate in the final titration is equivalent to 1 mole of oxygen in the sample.

Oxygen electrode method for dissolved oxygen measurement:

The oxygen electrode method (Fig.1) is used both for field measurement of dissolved oxygen and in the laboratory for determination of biochemical

oxygen demand. The oxygen electrode is based on voltammetric principles and depends on the diffusion and reduction of oxygen. The cell has a lead anode and a silver cathode set close together in an alkaline solution, often with 1M KOH. At the anode, the reaction is

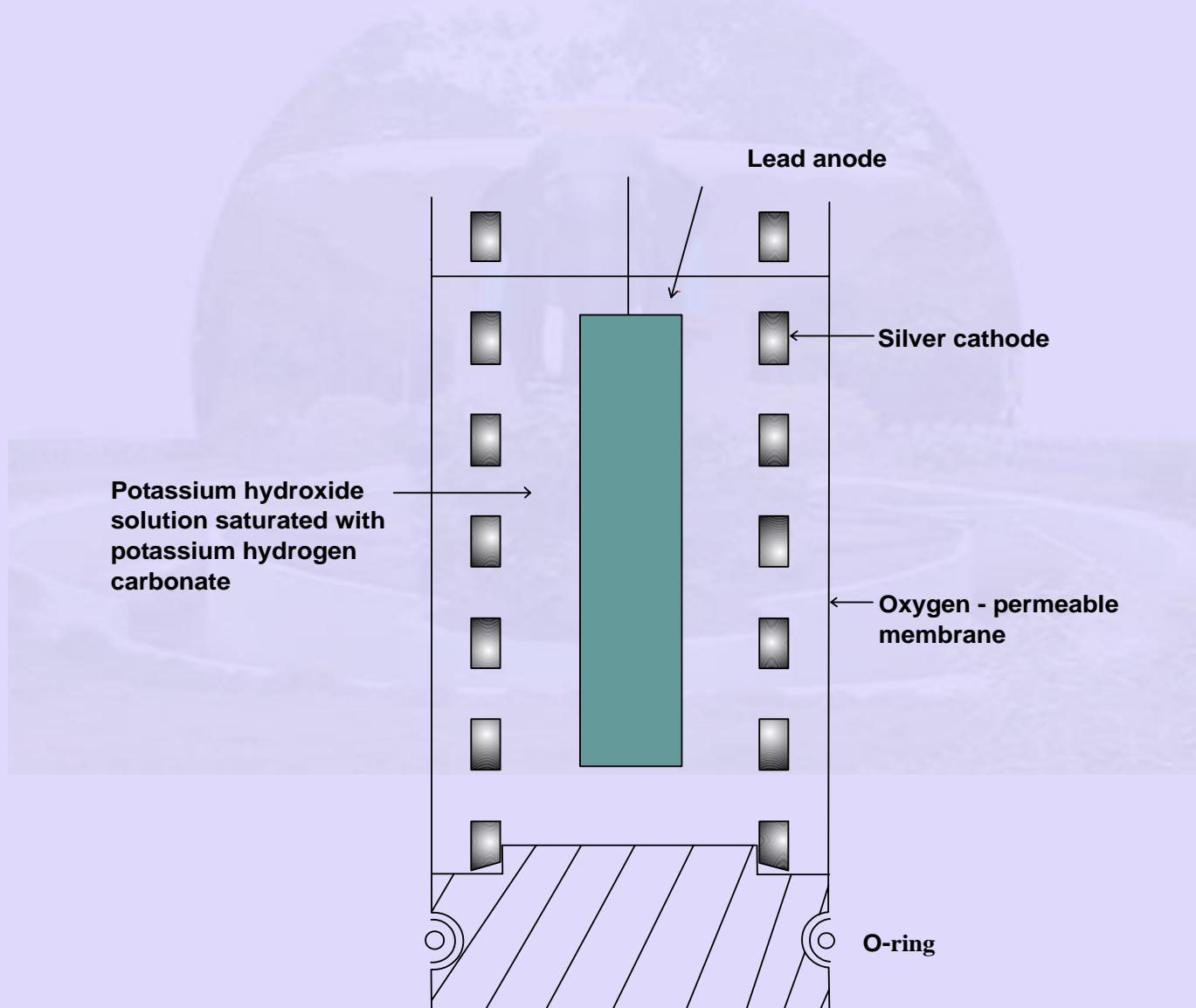
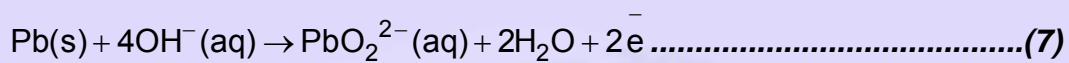


Fig.1 Oxygen electrode

(Redrawn by permission of John Wiley & Sons Ltd, Chichester, England, 779777 from Environmental analysis by Roger N. Reeve and John D. Barnes, p.59,1994)

The silver cathode is inert, unless oxygen or another reducible species can diffuse to it. A semipermeable membrane through which only oxygen can diffuse surrounds the electrodes, and then the reduction takes place.



Since current depends on the diffusion of oxygen to the electrode from the external solution, this electrode may be used to measure dissolved oxygen.

Instruments usually read oxygen directly with a scale from 0 to 100% saturation by setting 100% with fully aerated water and 0% with water no oxygen content (sodium sulphite is added to the water). This calibration must be made each time the electrode is used. Dissolved oxygen electrodes are very sensitive to temperature, and thus accurate temperature measurements must be made along with dissolved oxygen measurements so that a correction can be applied.

Oxygen demand:

Apart from rise in temperature, dissolved oxygen levels can be depleted by the biochemical breakdown of organic materials present in water. This latter can be greatly increased by discharges from industrial and agricultural sources. The most widely used and accepted measure of biodegradable organic content of waste water is the 5-day, 20°C BOD value. The brief analytical procedure is outlined below.

Measurement of biochemical oxygen demand (BOD):

Two 300ml bottles are filled with water sample and dissolved oxygen of the first bottle is determined immediately by either of the methods already

described. The second bottle is incubated under 20°C (adjusted to pH between 6.5 and 8.5 in the dark under standard conditions) for 5 days which are designed to be ideal to promote microbial activity and the dissolved oxygen is once more measured. The difference between the two DO values is the amount of oxygen that is consumed by microorganisms during the 5 days and is reported as BOD₅ (5-day BOD) value of the sample.

Typical BOD values for unpolluted water are of the order of a few mg l⁻¹. The BOD values of the effluents from some industries are shown in **Table.1**. It may be recalled that the saturated oxygen level of water is of the order of 8mg l⁻¹ and that the introduction of a small quantity of high-strength effluent can deplete the oxygen in many times its own volume of water.

Table 1

BOD values of effluents from some industries

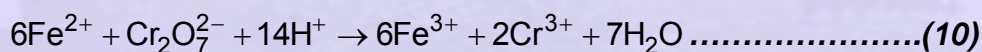
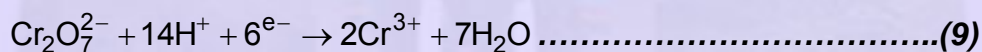
Effluents from	BOD in mg l⁻¹
1. Domestic wastes	800-2000
2. Dairy Wastes	800-4000
3. Farm yard wastes	1500-3000
4. Paper pulp	3000-27,000
5. Pharmaceutical	800-10,000
6. Wool scouring	800-10,000

The advantage of BOD measurement is that it parallels the natural processes closely, although it is a lengthy measurement to complete. A more

rapid measurement may be obtained by measuring the amount of chemical oxidation produced by acid potassium dichromate.

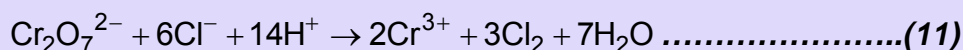
Measurement of Chemical oxygen demand (COD) :

In the COD test, the oxidising bacteria of the BOD test are replaced by a strong oxidising agent under acidic conditions. A sample of waste water containing organic material is mixed with an excess of potassium dichromate and sulphuric acid and the mixture is heated under total reflux conditions for a period of two hours. During digestion, the chemically oxidisable organic material reduces a stoichiometrically equivalent amount of dichromate; the remaining dichromate is titrated with standard ferrous ammonium sulphate solution.



Silver sulphate may be added as a catalyst for the oxidation of alcohols and low molecular mass acids.

Chloride ions that may be present in the water sample also consume dichromate according to the following reaction .



The interference of chloride is overcome by the addition of mercuric sulphate, which forms a chlorocomplex. The amount of potassium dichromate reduced gives a measure of the amount of oxidisable organic material. Dichromate has advantages over other oxidants and is applicable to a wide variety of samples.

The oxidation by oxygen can be represented by



1 mol of $\text{Cr}_2\text{O}_7^{2-}$ consumes 6 mol of electrons to produce 2 mol of Cr^{3+} . Since each mole of O_2 can consume 4 mol of electron to make H_2O , then 1 mole of $\text{Cr}_2\text{O}_7^{2-}$ is equivalent to 1.5 mol of O_2 .

The COD test is much more useful than the BOD test for estimating the oxygen requirements of certain industrial wastewaters. It is valuable for wastes where BOD test is not applicable due to the presence of toxic substances, low rate of oxidation, or other similar factors. BOD tests however are useful for long term monitoring of natural water.

On the basis of the above comparisons it can be suggested that BOD tests can be applied for long term monitoring of natural water and COD tests can be applied for rapid analysis of heavily polluted samples, e.g. industrial effluents.

Measurement of total organic carbon (TOC):

Both BOD and COD give indications of the oxidisability and oxygen demand of water samples. Neither, however, measures the total organic content of water. When this is required a determination of total organic carbon (TOC) is made. This is done by quantitatively oxidising all the organic matter in the sample to carbon-di-oxide soon after acidification to remove interference from carbonates or bicarbonates. Oxidation in a gas stream passing through a heated tube or wet oxidation with potassium peroxodisulphate have both been used. The latter is less convenient, but more sensitive and can be used at low levels below 1 mgdm^{-3} . The carbondioxide produced is measured either by conductivity after

absorption in solution or by catalytic conversion to methane which is then passed to a flame ionisation detector as used in gas chromatography.

The TOC test can be performed in a relatively short period of time (few minutes) compared to BOD and COD measurements and, hence offers a valuable supplement to BOD and COD estimations.

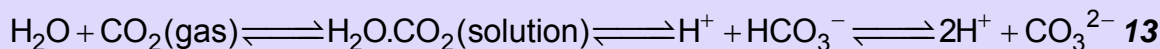
pH, Acidity and Alkalinity:

The pH of a water sample measures its hydrogen ion concentration and indicates whether the sample is acidic, neutral or basic. The pH may be measured accurately using a pH meter. The pH meter must be calibrated before making pH measurements. For calibration standard buffers of pH 4.00, 7.00 and 10.00 are used.

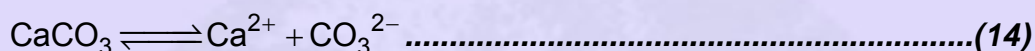
Table.2 pH ranges for environmental waters

Type of water	pH range
Soft water	5.3-7.4
Hard water	7.6-8.8
Sea water	8.2-9.2
Water affected by acidic pollutants	2.2-4.8
pH of water in equilibrium with atmosphere	5.6

It should be noted that the unpolluted rain water is slightly acidic due to the presence of dissolved carbon dioxide (pH=5.6). The range of pH values of hard and soft water samples are also shown in Table.2.



Hard water is slightly alkaline. The hardness is due to the presence of polyvalent metal ion, e.g. Calcium and magnesium arising from dissolution of minerals. For instance, the dissolution of limestone involves the following equilibria:



The change of pH of fresh water to acidic condition has a profound biological effect on the aquatic organisms. For example the population of salmon start to decrease below pH 6.5, perch below 6.0 and eels below pH 5.5 with little life possible below pH 5.0. Thus the eradication of life can result from a change of little more than 1 pH unit.

Acidity:

Acidity of water measures its quantitative capacity to react with strong base to a designated pH. The rates of chemical reactions, biological processes and corrosivity are all influenced by acidity of the water sample. Traditionally standard acidity is measured by titration with standard NaOH to end point of pH 3.7 or 8.3. The former is known as methyl orange acidity and the latter phenolphthalein acidity or total acidity.

Alkalinity:

Alkalinity measures the acid-neutralising capacity of water. It is attributed to the presence of hydroxide, carbonate, and bicarbonate ions in the

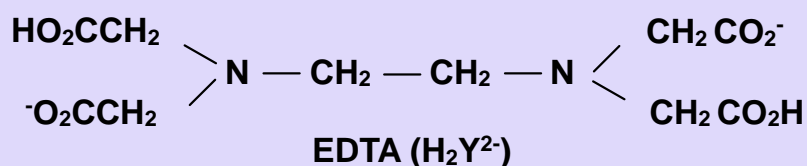
sample. Weak bases such as phosphates, silicates and borates may also contribute to alkalinity. Alkalinity is measured by titrating a measured volume of a sample of water against a standard acid solution to a designated end point usually pH 8.3 (phenolphthalein alkalinity).

Determination of water hardness:

The hardness in water is derived largely from contact with the soil and rock formations. Rain water as it falls upon the earth is incapable of dissolving the solids found in natural waters. The ability for the rain water to dissolve is gained in the soil where CO₂ is released by the bacterial action. The dissolved CO₂ in rain water is sufficiently acidic to attack the insoluble carbonates in the soil and lime stone formations converting them to soluble bicarbonates. Since lime stone is not pure carbonate, but includes impurities such as sulphates, chlorides and silicates, these materials become exposed to the solvent action of water as the carbonates are dissolved and they pass into solution too.

In general, hard waters originate in areas where top soil is thick and lime stone formations are present. Soft waters originate in areas where the top soil is thin and lime stone formations are sparse or absent.

Analysis is normally performed by complexometric titration using the disodium salt of ethylene diamine tetra acetic acid (EDTA).



This forms as 1:1 complex with divalent metal ions:



To determine both calcium and magnesium by titration, the pH has to be buffered at 10. The end-point is detected using an indicator such as Eriochrome Black T.

The total hardness is conventionally expressed in mg l^{-1} units as calcium carbonate, even if it is due to calcium sulphate, magnesium carbonate or any other polyvalent metal salt.

The total hardness is calculated using the relationship. 1000 ml of 0.01M EDTA \equiv 100mg CaCO_3 . By titrating a known sample of water and knowing the titre value of the standardised EDTA and its molarity, can be calculated. The terms "hard water" and "soft" water may be defined within very specific concentration ranges as shown in the following **Table 3**.

Table: 3 Assessment of water

$\text{mg l}^{-1}(\text{CaCO}_3)$	Assessment
0-50	soft
50-100	moderately soft
100-150	slightly hard
150-200	moderately hard
200-300	hard
>300	very hard

Total dissolved solids-by conductivity measurement:

The concentration of total soluble inorganic content of a water sample can be measured by evaporating a known volume of the water sample to dryness

and finding the weight of the solid. A much simpler and quicker way of determining the dissolved solids is by the conductivity cell method. It consists in dipping the cell in water to be tested. It consists of two electrodes often platinum, coated with platinum black separated by a fixed distance. These electrodes are connected to a conductance meter, or more simply a wheatstone bridge and the conductance is measured directly. In order to prevent electrolysis taking place, which would change the concentration of the solution, the bridge uses a low voltage alternating current. Plastic and flow through conductance cells are also available.

The resistance of the liquid between the electrodes is measured, which is converted into conductivity using the relation.

$k = L / AR$ where k = conductivity; L = distance between electrodes (cm);
 A = surface area of electrodes (cm^2); R = resistance (siemens, S)

The units of conductivity applicable to environmental samples are $\mu\text{s cm}^{-1}$, a typical value of $200 \mu\text{s cm}^{-1}$ being found for water with a substantial ionic salt content.

Using the solution of known conductivity, the cell is calibrated. Care has to be taken that calibration solution and the unknown sample are at the same temperature, since the conductivity is highly temperature dependent.

The general assumption that all ions having the same charge have approximately the same conductivity will not hold good in the case of environmental water samples. Since most environmental water samples contain ions with different charges in varying concentrations. However the following

approximate equation gives the total concentration of salts with a reasonable accuracy.

Total salt concentration = $A \times \text{Conductivity (mg l}^{-1}\text{)}$ where A is a constant in the range 0.55 – 0.80.

