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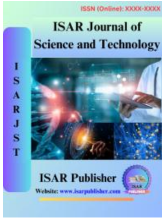

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A MINI REVIEW ON WATER QUALITY ASSESSMENT METHODS FOR CATIONS AND ANIONS IN NATURAL WATER SOURCES

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Abstract: The purpose of this article is to review on few parameters of water quality assessment methods like pH, alkalinity, salinity, hardness, conductance etc. commonly employed. Various methods have been discussed which are employed to analyze cations and anions in natural sources of water, which are key indicators of water quality. The major cation such as Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Sodium (Na^{+}), and Potassium (K^{+}) and anions such as carbonate (CO_3^{2-}), bicarbonate (HCO_3^{-}), Chloride (Cl^{-}), Fluoride (F^{-}), Arsenate (AsO_4^{3-}), Sulfate (SO_4^{2-}), nitrate (NO_3^{-}), and phosphate (PO_4^{3-}) significantly influence the chemical balance of water system. In this review, we have discussed some analytical methods for few cations and anions present in water sample. The permissible limits of these ions present in water sample are also discussed according to Indian Council of Medical Research (ICMR) and World Health Organization (WHO) standards for drinking purposes. The review is mainly on the different parameters for the quality measurement of water for drinking purposes, respectively. The review highlights the strengths and limitations of each method, and discusses the growing need for integrated approaches that combine chemical, physical, and biological assessments to achieve comprehensive water quality evaluation. Understanding the concentration and distribution of cations and anions is essential for managing water resources, mitigating pollution, and ensuring public health safety.

Keywords: Water Quality, Cations, Anions, Salinity, Alkalinity, Hardness, Fluoride, Arsenate.

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Introduction

Water is perhaps the most precious natural resource after air. Water is the basic requirements of all life exist on earth. It also plays an important role for the purpose of drinking, irrigation, and aquaculture and livestock usages. Water is the foundation of our existence. It is impossible for life to function without water or needless to say that without enough good water our survival will be threatened. We may be able to survive without food for a whole week but without water we won't even survive for 3 days. It has vast usages on daily purposes as usual from drinking to washing face to taking bath etc. and also in cleaning food processing or manufacturing industrial factories, as coolant, and agriculture fields etc. (Baruah et al., 2005).

Though the surface of the earth mostly consists of water, only a small part of it is useable, which makes the resource limited and precious. About 71%of the earth surface is consist of water and 21% land but apart from this water occurs 97.7% in ocean as salt water which is unfit for daily usages, 2.09% in icecaps and glaciers, 0.6% ground water, 0.11% run off and surface water. The figure 1 shows the distribution of water on earth.

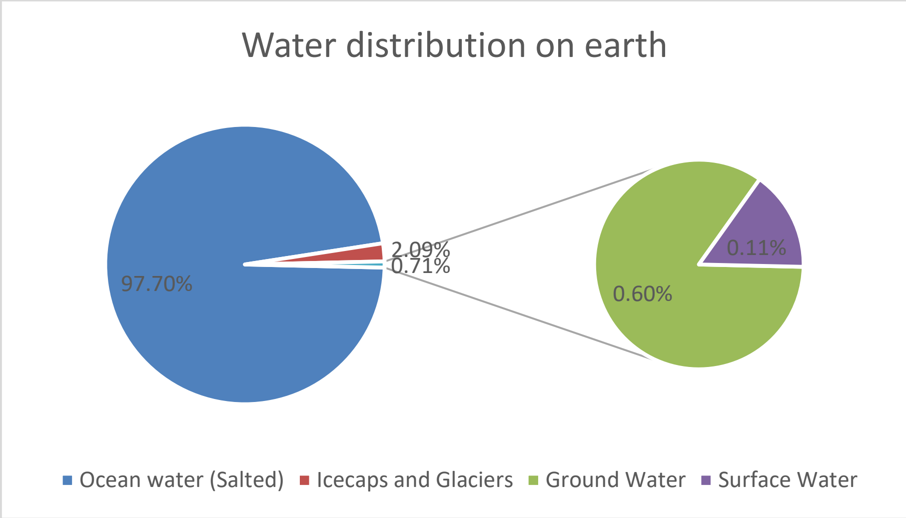

Fig 1: Distribution of water on earth.

Hence, the available water that is directly useable for substance should be wisely used and also should be protected from contamination. In this world, clean and safe water for drinking is one of the important basic needs for the continuity of human beings on earth. However, its vast abundance, water is very much limited. It is a non–renewable resources. In addition, we required to realize the fact that although there is an abundance of water. In other words, a world without water resources is exceedingly decreasing due to distu8rbance caused by human race. In addition to this, occurrence of various types of pollutants, including the heavy metals, introduced to water through natural or anthropogenic activities causes toxic and harmful effects to the individuals and the environment (Braun et al., 1993).

India is huge user of ground water in the world. It uses an estimated 230 cubic kilometers of groundwater per year over a quarter of the global total. More than 60% of irrigated agriculture and 85% of drinking water supplies are dependent on groundwater. Urban residents increasingly depend on groundwater due to unreliable and inadequate municipal water supplies. Groundwater act as a critical buffer against the variability of monsoon rains. For example, a rainfall deficit in 1963 to 1966 decreased India's food production by 20%. But a similar drought in 1987-88 had very small impact on food production largely due to the wide spread use of ground water by that time. Groundwater in India is acritical resource. However, an increasing number of population and aquifers are reaching unsustainable level of exploitation. If current trends in 20 years, about 60% of all India's aquifers will be in critical condition says a World Bank report, deep wells and prudence. This will have serious implication for the sustainability of agriculture, long term food security livelihoods and economic growth. Groundwater in India is acritical resource. However, an increasing number of aquifers are reaching its estimated that5v over a quarter of countries harvest will be at risk. Farms irrigated with ground water have twice the crop water productivity of those that rely on surface water alone. Thus, is largely because the resource allows farmers greater control over when to irrigate their fields and how much water to use each time. Despite the valuable nature of the resource, 29% of ground water leads are semi critical, critical, or overexploited, and the situation is the deteriorating rapidly. Moreover, aquifers are depleting in the most populated and economically productive areas. Climate change will further strain ground water resources. This will have serious implications for the sustainability of agriculture, long term foods security livelihoods, and economic growth. It is estimated that over a quarter of country harvest will be at risk. A complex wave of factors determined ground water extraction: the size of the land holdings, density of population, water intensity of crops planted, water user's behavior, legislation an administration of ground water, power subsidies for pumping irrigation water, an economic policy. India has both hard rocks and alluvial aquifers which differs considerably both the micro and macro levels. As global experience offers few comparable models, home ground solutions are need.

Permissible Limits of Various Parameters

The quality of drinking water should be determined with respect to a large number of parameters to insure the supply of safe drinking water to masses. By carefully monitoring's the water quality parameters, it may be possible to understand the interaction among the various constituents and waters and to arrive at some valid conclusions about the water quality that impacts all form of lives, both terrestrial and aquatic. The present study, however confirm to only those parameters for which experimental facilities exist (Tanaka et al., 2001). These are:

Physical parameters	Colour, Odour, Turbidity, pH, conductivity
Major anions:	Alkalinity (carbonate and bicarbonate), Chloride, Fluoride, Arsenate
Major cations:	Calcium, Magnesium, Iron

In figure 2, we have shown different parameters that are used for assessment of water quality which can be used for different as drinking water, domestic water, industrial water and irrigation water.

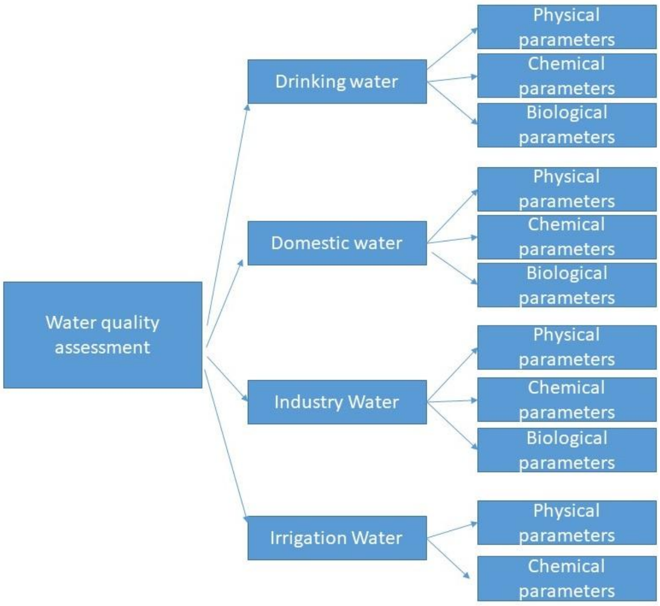

Fig 2: The parameters that used for water quality assessment for different purpose.

Physical Parameters:

pH:

The pH of any aquatic system is an important indicator of water quality and the extent of pollution in the basic area. Due to the presence of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions in solution, the pH of most natural water lies between 6.5-8.5, but values lower than the minimum limit may be due to the presence of dissolved carbon dioxide and organic acids (fulvic and humic acids), derived from the decay and subsequent leaching of plant materials. This may also be related to the wide distribution of lateritic soil whose pH is always acidic. The low pH could be related to use of acidic producing fertilizers like ammonium and super phosphates of line. Water with pH<6.5 can be corrosive towards metals pipes in the water distribution system in the households, which in turn maybe dissolve toxic metals such as zinc, lead, cadmium, copper, etc. and spread them throughout the system. Further, low pH water may cause gastrointestinal disorders like hyperacidity, ulcers, and stomach pain with burning sensation.

Electrical Conductivity:

Electrical conductivity (EC) values are useful indicators of the dissolved solids having the capacity to conduct the electrical current and they can be utilized as a base for extrapolating other chemical data when only partial chemical analysis is possible (Kumar & Puri, 2012). The importance of electrical Conductivity is its measure of salinity which greatly affects the taste and thus has a significant impact on the user acceptance of their water potable. It is mostly influenced by aquifers material, solubility of minerals, duration of contact and factors such as the permeability of soil, drainage facilities, quantity of rainfall and also, climate of the area.

Hardness:

It is important parameters in estimating water quality whether it is to be used for domestic, industrial or agricultural purpose. The total hardness is dependent on the presence of $Ca^{2+}$and Mg^{2+} contents that enter the water bodies through residues of soaps, detergent and parent bad rock materials made up of Ca^{2+} and Mg^{2+} and other metal ions. It prevents lather formation with soap and increases the boiling point of water. The major cations imparting hardness are calcium and magnesium and the anions are bicarbonates, carbonate sulphates, and chloride. Hardness is temporary if it is associated with carbonates and bicarbonates and permanent if with sulphates and chlorides. Other contributors to large hardness values might have been additions of large quantities of sewage, detergents and other domestic wastes by the run off during heavy rain. Drinking of extremely hard water leads an incidence of urolithiasis. However, there is no farm evidence that water hardness causes any ill effect in man (Ramires et al., 1995).

Major Anions:

- **Alkalinity (Carbonates and Bicarbonates):**

The presence of carbonates, bicarbonates, and hydroxides are the main cause of alkalinity in concentration.

- **Chloride:**

Chloride occurs naturally in all types of water in widely varying concentration. The origin of chloride in water may be from diverse source such as weathering and leaching of sedimentary rocks and soils, domestic, and industrial waste discharge, etc. Excessive chloride in potable water is not particularly harmful and the quality criterion recommended for this is based primarily on palatability considerations and its potentially high corrosive character.

- **Fluoride**

Fluoride amounts from the action of carbonates upon the basic materials in the soil. The bicarbonate in water system is likely to have come from the atmospheric carbonate dioxide, soils and dissolution of carbonate rocks. However, bicarbonate content is largely determined by CO_2 water equilibrium followed by generation of carbonic acid, H_2CO_3 that interacts with the primary minerals increasing the bicarbonates (Moeinzadeh et al., 2024).

According to WHO (1984) and Indian standard drinking water specification 1991 the maximum permissible limit of fluoride in drinking water 1.5ppm and highest desirable limit is 1.0 ppm. Fluoride concentrations above 1.5 ppm in drinking water cause dental fluorosis and much higher concentration skeletal fluorosis. Low concentration (approximately 0.5 ppm) provides protection against dental caries. India is among the 23 nations around the globe where health problems occur due to the consumption of fluoride contamination water and the extent of fluoride contamination in water varies from 1.0 to 400 mg/l. In India, 20 million people are severely affected by fluorosis and 40, million people are exposed to risk pf endemic fluorosis. In India fluoride endemic states are Andhra Pradesh, Karnataka, Tamil Nadu, Punjab, Haryana, Maharashtra, Gujarat, Rajasthan, Uttar Pradesh Kerala Jammu and Kashmir and Delhi (Li et al., 2013).

- **Arsenate:**

Arsenate (AsO_4^{3-}) is an oxyanion of arsenic and a common contaminant found in natural and human-impacted water systems. It is the pentavalent form of arsenic (As^{5+}) and is chemically similar to phosphate (PO_4^{3-}), which allows it to interfere with biological processes in aquatic systems (Kalita et al., 20210). Different sources of Arsenate in Water such as

1. Natural Sources: Weathering of arsenic-containing rocks and minerals and Volcanic activity.

2. Anthropogenic Sources: Use of arsenical pesticides and herbicides, Mining and smelting operations, Industrial discharges, Combustion of fossil fuels etc.

The Arsenate shows stable behavior under oxidizing conditions in Water Systems. However, in reducing environments, arsenate can be converted to arsenite (As^{3+}), which is more toxic and mobile. It also competes with phosphate for adsorption sites on mineral surfaces, particularly iron oxides. It exists in various protonated forms depending on pH (e.g., $H_2AsO_4^-$, $HAsO_4^{2-}$).

As we know the long-term exposure to arsenate-contaminated water can lead to skin lesions, cancers, cardiovascular diseases, and developmental effects. It can also affect aquatic organisms by interfering with energy metabolism and enzyme function.

The World Health Organization (WHO) and U.S. Environmental Protection Agency (EPA) set the maximum allowable concentration of arsenic (including arsenate) in drinking water at 10 µg/L.

Major Cations:

- **Calcium and Magnesium:**

Calcium and magnesium are the ions determining total hardness and hence are interrelated (Silverstein & Heller, 1997). Generally, calcium and magnesium maintain a state of equilibrium in most waters. High values may occur due to the seepage of effluent and domestic wastes or due to cationic exchange with sodium. However, low values do not mean that it is not influenced by the pollutants but it might be due to the reverse cationic exchange with sodium (Ca and Mg ions replaced by sodium's). Calcium is the fifth among the elements in order to abundance and its presence in natural waters due to leaching from limestone, dolomite, gypsum and gypseous shale. A sewage and industrial waste disposals are also important sources of calcium in the aquatic environment. The common source of magnesium in the groundwater is dolomite in the sedimentary rocks. Magnesium is also a common constituent of natural water, the concentrations of which generally remain lower than that that of calcium. Various kinds of rocks, sewage and industrial wastewater are the principal sources of magnesium (Gholizadeh et al., 2016).

- **Iron**

Iron (Fe) is a common element found in natural water systems, typically present as either ferrous (Fe^{2+}) or ferric (Fe^{3+}) iron (Butt & Riaz, 2009). Although essential for many biological processes, excessive iron can affect water quality, aquatic life, and infrastructure (e.g., staining, clogging of pipes). Assessing iron concentration and speciation in water is crucial for environmental monitoring and water treatment (Uddin et al., 2015).

Forms of Iron in Natural Waters

1. **Dissolved Iron:**
    - **Ferrous iron (Fe^{2+}):** Soluble under reducing (low oxygen) conditions.
    - **Ferric iron (Fe^{3+}):** Precipitates as iron oxides or hydroxides in oxidizing conditions.
2. **Particulate or Colloidal Iron:**
    - Bound to suspended solids or organic matter.
    - Often in the form of iron oxides or oxyhydroxides.

Assessment of iron in natural water systems requires careful sampling and appropriate analytical methods depending on the form and concentration of iron. Colorimetric and spectroscopic methods are the most common, while advanced techniques like ICP-MS offer high sensitivity for trace-level analysis. Accurate iron assessment helps manage water quality and environmental impacts effectively.

In table 1, we have shown permissible limits of various parameters of water according to WHO and ICMR. Based on which the water treatment are done at different levels.

Table 1: Permissible limits of various parameters of water according to WHO and ICMR:

Parameters	Unit	Permissible limits	
		WHO	ICMR
pH	no unit	6.5-8.5	6.5-8.5
Conductivity	µS/cm	1000-2000	300
Ca^{+2}	mg/L	100	75
Mg^{+2}	mg/L	150	30
Iron	mg/L	0.3	0.3
Alkalinity	mg/L	200	200
Salinity	mg/L	600	-
Arsenic	mg/L	0.01	0.05
Total Hardness	mg/L	500	600
Fluoride	mg/L	1.5	0.6-1.2

Assesment Methods for Water Quality Determination:

Determination of pH

The term pH refers to the measurement of hydrogen ion activity in the solution. Since the direct measurement of the pH is very difficult, specific electrodes are needed for quick and accurate pH determination. pH is measured on a scale of 0 to 14, with lower values indicating high H^+ (more acidic) and higher values indicating low H^+ ion activity (less acidic). A pH of 7 is considered as neutral. Every whole unit in pH represents a ten-fold increase in or decrease in or decrease in hydrogen ion concentration. Most natural waters possess the pH values ranging from 5.0 to 8.5. Rain water have a H^+ ion concentration and thus the water may become alkaline with a pH of 8.0-8.5. More acid water (pH=9) and other immediate changes in the hydrogen ion concentration (pH) suggest that the quality of the water is adversely affected due to introduction of some toxic contaminants in water bodies. Before measurement pH in Digital pH meter, the meter should be calibrated. In figure 3, we have shown the representative diagram to measure the pH of water sample.

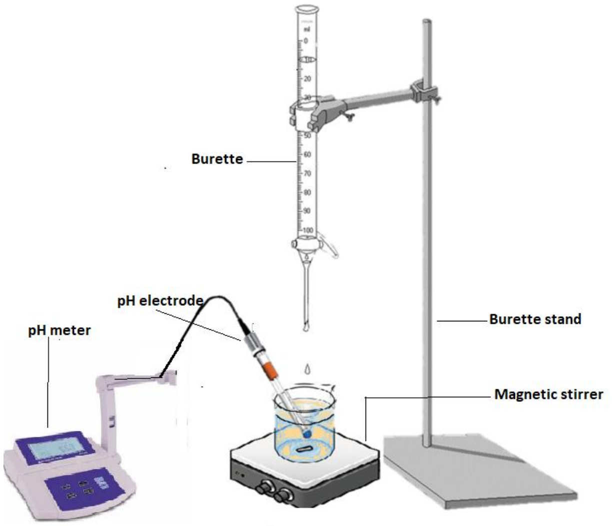

Fig 3: The representative diagram to measure the pH of water sample.

Determination of Alkalinity

1. The mixtures are titrated with a standard solution of HCL or H_2SO_4 by the selective use of indicators with the reactions proceed in the following ways (Tirkey et al., 2013)

$$\mathbf{NaOH + HCl \rightarrow NaCl + H_2O}$$

$$\mathbf{Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3}$$

This $NaHCO_3$ further react with HCl

$$\mathbf{NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O}$$

The phenolphthalein is added as first indicator which loses its colour of alkaline medium when NaOH and half Na_2CO_3 are neutralised. In fact, it does not give colour in $NaHCO_3$ solution. Methyl orange act as second indicator which is used to show the complete neutralization.

Determination of Salinity

Salinity refers to the total amount of soluble salts dissolved in a kilogram of water collectively (Saad et al., 1998). The salts in water include such common ions as $Ca^{+,}$ Mg^{2+}, $K^{+,}$ Na^+, Cl^-, SO_4^{2-} HCO_3^- and CO_3^{2-}. These occur either naturally or added as pollutants to the environment. The titrimetric method can be regarded as accurate enough, although the method assumes that the percentage composition of chloride in sea water is constant in relation to all other dissolved minerals present, Salinity can be determined by titrimetric method by titrating the water sample with $AgNO_3$, using potassium chromate it colour turns from yellow to brick red colour.

The reaction involve in determination of salinity involves:

1. Primary reaction involves Chloride precipitation

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ (a white precipitate of silver chloride forms.)

2. Indicator Reaction (Endpoint Detection):

Once all Cl^- ions are precipitated, additional Ag^+ reacts with chromate ions (CrO_4^{2-}):

$2Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s)$ (a red-brown precipitate of silver chromate indicates the endpoint.)

Determination of Hardness

Hardness of water is determined by titrimetric method by titrating with a standard solution of ethylenediaminetetraacetic acid (EDTA) which is a complexing agent. Ammonium buffer solution and EBT indicator can also be used. Since EDTA is insoluble in water, the disodium salt of EDTA may be taken for experiment. Adding 2-3 drops of buffer solution and a pinch of EBT indicator to the water sample it gives a red wine colour. Titrating the sample water with EDTA the sample colour changes to blue from red wine (Tyagi et al., 2013).

EDTA can form four or six coordination bonds with a material ion. Two type of hardness is present in water first is temporary hardness and second is permanent hardness. Temporary hardness is due to the presence of bicarbonates of calcium and magnesium. It can be easily removed by boiling. Permanent hardness is due to the presence of chlorides and sulphates of calcium and magnesium ions.

Conclusions

The main focus of this review is on parameters of water quality assessment like pH, alkalinity, salinity, hardness, conductance etc. and various methods that has been discussed which are employed to analyze different cations and anions present in water system, which are key indicators of water quality. The major cation such as Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Sodium (Na^+), and Potassium (K^+) and anions such as of carbonate (CO_3^{2-}), bicarbonate (HCO_3^-), Chloride (Cl^-), Fluoride (F^-), Arsenate (AsO_4^{3-}), Sulfate (SO_4^{2-}), nitrate (NO_3^-), and phosphate (PO_4^{3-}) significantly influence the chemical balance of water system. The permissible limits of these ions present in water sample are also discussed according to Indian Council of Medical Research (ICMR) and World Health Organization (WHO) standards for drinking purposes. The review highlights the strengths and limitations of each method, and discusses the growing need for integrated approaches that combine chemical, physical, and biological assessments to achieve comprehensive water quality evaluation. Understanding the concentration and distribution of cations and anions is essential for managing water resources, mitigating pollution, and ensuring public health safety.

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