Measurement of pH *and electrical conductivity (EC) groundwater*

Girdhari Lal Meena

Assistant Professor of Chemistry
Govt. PG College Rajgarh (Alwar)

Introduction

Measurement of pH of groundwater sample: The pH of groundwater is anextent of the total quantity of hydrogen ions. It determines the nature of water whether it is acidic or alkaline. According to WHO, the value of pH for water is ranging from 6.5 to 8.5 (pH in drinking water, WHO, 2007). In this study, the pH of water has been determined by the electrometric method with the help of a pH meter, which is extensively used for the determination of hydrogen ion (H^+) concentration in water samples (Manual on pH, Systronics, 2003; Guidelines for Drinking water quality, 1997; Khurana and Sen, 2005). It is one of the most accepted methods in the research laboratory for the determination of H^+ ion concentration (pH) of water with high accuracy in pH value of 0.1 to 0.0001.

- **Principle of electrometric method for determination of pH:** The basic principle of the electrometric method for the purpose of pH is the determination of H^+ ion activity through potentiometric measurement exploiting a "Combined standard hydrogen electrode" and a "Reference electrode". The electrode potential difference across these electrodes will give the H^+ ion concentration (pH) of a solution.
- **pH measurement apparatus:** Electronic pH meter with an attached electrode and thermometer.
- **Reagents:** Standard pH buffer solutions were employed for the standardization of pH meter.
- **Procedure:** The detailed procedure for measuring the pH of the water sample considering the following steps:

(i) We switch on the pH meter and cleaning the glass electrode with distilled water.

(ii) Now we standardize the pH meter by standard buffer solutions of known pH values. For the calibration of pH meter, glass electrode was first placed in pH 7.0 standard buffer solution and then adjusted the pH meter accordingly. The glass electrode was rinsed with distilled water and transferred it to pH 4.0 standard buffer solution and then further adjusted the pH meter accordingly. The same procedure was repeated for pH 9.2 standard buffer solution. The above procedure was repeated to ensure that the pH meter has been calibrated accurately and ready to use for the pH measurement of the unknown water sample.

(iii) After successful calibration, we clean the glass electrode with distilled water and carefully wiped with a tissue paper to make sure that the glass electrode is clean before pH measurement of the water sample.

(iv) About 75 mL of groundwater sample was taken in a 100 mL beaker confirming that the glass electrode was completely dipped into the water sample. We agitate the solution and wait for few seconds to steady the reading and then record the pH of groundwater sample.

We repeat step **(iii)** and **(iv)** for every new groundwater sample's pH measurement. All groundwater sample's pH value recorded at 25°C temperature.

Measurement of electrical conductivity (EC) of groundwater sample: The electrical conductivity (EC) of water is certainly a measurement of salinity and it is a numerical expression of water or an aqueous solution to carry electrical current. This ability depends on the total concentration of dissolved solids, mobility of ions and temperature of the water. EC indicates the total concentration of the ionized ingredients of water samples. It can be measured with the help of a conductivity meter. The measurement of EC will give the total concentration of dissolved salts in water samples.

- **Electrical conductivity measurement apparatus:** Conductivity meter, graduated cylinder of 100 mL capacity and beaker.
- **Reagents:** 0.01N KCl aqueous solution.
- **Procedure:** The detailed procedure for measuring the EC of the water sample considering the following steps:

(i) We switch on the conductivity meter, clean the conductivity cell with distilled water and allow it to calibrate with a 0.01N KCl solution. It gives an EC of 1413 μS/cm at 25°C.

(ii) After calibration, we clean the conductivity cell with distilled water to make sure that the conductivity cell is clean before the EC measurement of the water sample.

(iii) After that we dip the conductivity cell in the groundwater sample and record the EC of the water sample at 25°C.

We repeat step **(ii)** and **(iii)** for every new groundwater sample's EC measurement.

Determination of total dissolved solids (TDS) of groundwater sample: Total dissolved solids (TDS) of water indicates the total concentration of dissolved ingredients in water which is made up of inorganic substances with small amounts of organic substances. The most common inorganic substances which are found in water constitutes cations (Ca, Mg, Na, K etc.) and anions (Chlorides, Fluorides, Sulfates, Carbonates, Bicarbonates, Nitrates, etc.). The determination of TDS of the water sample has been carried out by the electronic method, which is moderately consistent. The conductivity bridge is an extensively used method for the purpose of conductivity of the water sample and EC is correlated to the TDS of water.

- **Principle:** The conductivity is usually determined by a modified Wheatstone bridge. The output of Wheatstone bridge is fed to an amplifier null detector. This method is used to determine TDS in the water sample by the capacity of "Specific conductivity" with a conductivity probe that observes the occurrence of ions in water. After measuring the specific conductivity (µS/cm) of the water sample, TDS of the water sample can be calculated using the following equations:

$$Specific\ conductivity = Multipler\ reading \times Dial\ reading \times Cell\ content$$

$$TDS\ (mg/L) = Specific\ conductivity \times Temp.factor\ (0.7)$$

- **TDS measurement apparatus:** Conductivity Bridge, conductivity cell and a thoroughly rinsed beaker.
- **Procedure:** To start the procedure, the Wheatstone bridge was switched on and allowed to stand for about a minute before starting the measurement. About 60 mL of the water sample was taken in a 100 mL beaker, ensuring that the conductivity cell is immersed about 1 cm below the surface of water sample. After that, the multiplier switch was turned step-by-step and set in between where the needle moved towards the null point. The dial disk was now adjusted for a null. When the pointer came to center the scale, it means the bridge was balanced. Now, recorded the dial reading and calculated the specific conductivity and TDS using the above-mentioned equations.

Determination of chloride in groundwater sample: Chlorides being highly soluble in water are present in all type of water, but the amount is frequently very low in natural water. The determination of Chlorides has been carried out by the Mohr's Titrimetric or Argentometric method in the present study. Karl Friedrich Mohr has been developed this method in 1986 (Vogel, 1964). This method involves silver nitrate ($AgNO_3$) titration with chromate indicator to determine the chloride ion concentration in the water sample (Vogel, 1964).

- **Principle:** Silver nitrate ($AgNO_3$) reacts with chloride ions to form silver chloride (AgCl) white precipitate.

$$Cl^- + AgNO_3 \rightleftharpoons AgCl \downarrow (White\ precipitate) + NO_3^-$$

Potassium chromate (K_2CrO_4) shows the brick red color at the endpoint of the titration due to the formation of silver chromate (Ag_2CrO_4). The K_2CrO_4 solution used as an indicator.

$$K_2CrO_4 + 2AgNO_3 \rightleftharpoons Ag_2CrO_4 \downarrow (Brick\ red\ colour) + 2KNO_3$$

If $pH > 8.3$ – $Ag(OH)_2$ is precipitated
If $pH < 7.0$ – $Ag_2Cr_2O_7$ is precipitated

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

- **Apparatus:**Pipette, Burette, Conical Flask etc.
- **Reagents:** Potassium chromate (K_2CrO_4) indicator,standard silver nitrate solution ($AgNO_3$; 0.0141N; 1 mL 0.0141N $AgNO_3$ = 0.5 mg Cl^-), and standard sodium chloride solution (NaCl, 0.0282N; 1 mL of 0.0282N NaCl = 1.0 mg Cl^-).
- **Procedure:** The detailed procedures for measuring the Cl^- ion concentration from water sample considering the following steps:

(i) We take 10 mL of the sample solution in conical flask followed by adding 2–3 drops of potassium chromate (K_2CrO_4).
(ii) The solution was then titrated with 0.0141N standard $AgNO_3$ solution until a brick red color was obtained and record the reading of $AgNO_3$ used at the endpoint of the titration.
(iii) We repeat the above titration with blank.
(iv) Finally, we calculate the chloride ion concentration in water sample using the following equations:

$$Chloride\ (mg.L^{-1}) = \frac{(X - Y) \times N \times 1000}{Volume\ of\ sample\ (mL)}$$

Where, X = $AgNO_3$ required for sample (mL); Y = $AgNO_3$ required for blank (mL); N = Normality of $AgNO_3$ used.
1000 mL of 1N $AgNO_3$ = 35.45 gm Cl^-
1 mL of 0.0141N $AgNO_3$ = 35.45 x 0.0141 mg Cl^- = 0.5 mg Cl^-.

Determination of fluoride in groundwater sample: Fluoride is naturally found in groundwater sources in high concentrations (Sharma et al., 2017). Well and bore-well water often contaminated with fluoride and sometimes it is also found in river and lake water as a result of industrial discharges (Slooff, 1988). Thus, all water sources are highly contaminated with fluoride. Fluoride ion concentrations in water have been examined electrochemically, using ion-selective electrode technique (APHA, 1989; Sareen, 1988; Sawyer and Parkin, 2003; Shankar et al., 2008). This technique applies to the measurement of fluoride in drinking water in between 0.1 - 1.000 $mg.L^{-1}$ concentration.

- **Principle:** The fluoride ion-sensitive electrode is the solid-state kind electrode, that comprising of a lanthanum fluoride crystal; in use, it forms a cell in combination with a reference electrode, normally the calomel electrode. The fluoride ion-selective electrode can be used to measure the activity or concentration of fluoride in an aqueous sample by use of an appropriate calibration curve. However, fluoride activity depends on the total ionic strength of the sample.
- **Apparatus:**Ion selective probe meter, fluoride sensitive electrode, reference electrode, stirrer, plastic lab wares etc.
- **Reagents:** Total ionic strength adjustment buffer (TISAB) and Standard fluoride solution (1 mL = 10 µg of F^- ion).
- **Procedure:** The detailed procedures for measuring the F^- ion concentration from water sample considering the following steps:

(i) We take 100 mL of fluoride standard solution (1.0 ppm and 10.0 ppm) and add 100 mL TISAB and calibrate the apparatus.
(ii) We transfer 50 to 100 mL of specimen solution to a 250 mL beaker.

(iii) We rinsed and dried electrode place in the specimen solution, stir carefully& note down the constant reading on the ion selective meter. Now rinsed the electrode with distilled water after completing the experiment.

Determination of nitrate in groundwater sample: Nitrate is also naturally present in drinking water in small amount and it is measured in theextent of nitrogen. Generally, nitrate (NO_3^-) ions were analyzed by UV-Vis spectrophotometric method(APHA, 1989; Sareen, 1988; Sawyer and Parkin, 2003). The methods used for measurement of nitrate in water are generally based on photometric investigation afterward the reduction to nitrite (NO_2^-) ion.

- **Principle:** The basic principle of the process is to measure nitrate ions in water by ultraviolet absorption at 220 nm for rapid nitrate analysis. The calibration curve for the nitrate follows Beer's Law up to 11 mg N/L. If organic matter dissolved in the sample, then it may also absorb at 220 nm and nitrate does not absorb at 220 nm. A second measurement can be made at 275 nm to correct the nitrate value. Acidification with 1N HCl is designed to prevent interference from hydroxide or carbonate concentrations up to 1,000 mg/L as $CaCO_3$.
- **Apparatus:** UV Spectrophotometer, use in between 220 nm to 275 nm with 1 cm path length silica cuvette, micro filter, and Nessler tubes (capacity – 50 mL).
- **Reagents:** Stock nitrate solution (0.5 mL = 50 µg N = 221.5 µg NO_3^- ion), std. nitrate solution (0.50 mL = 5 µg N = 22.15 µg NO_3^- ion), 1N HCl solution & aluminium hydroxide [$Al_2(OH)_3$] suspension.
- **Procedure:** The detailed procedures for measuring the nitrate (NO_3^-) ion concentration from water sample considering the following steps:

(i) **Color Removal:** Colored samples contain organic interference and to remove the color from the sample, we add 40 mL $Al_2(OH)_3$ suspension per liter sample solution in an Erlenmeyer flask. Now shake to thoroughly mixing and leave for 10 min then filter it over the membrane filter.

(ii) **Sample Treatment:** We take 100 mL of clear sample and add 2 mL 1N HCl and mix carefully.

(iii) **Preparation of standard calibration curve:** We prepare nitrate standard solutions for standardization in the range of 0 to 350 µg N by diluting to 50 mL with the volumes of the standard nitrate solution: 0.0, 1.0, 2.0, 4.0, 8.0, 16.0, 32.0 mL and the nitrate standards in the identical way as the samples.

(iv) **Spectrophotometric Measurement:** We record the absorbance alongside redistilled water set at zero absorbance. Now use a wavelength of 220 nm to get the nitrate reading and if needed, use 275 nm wavelength to get interference due to dissolved organic matter.

(v) **Calculation:** For adjustment of dissolved organic matter, subtract 2 times the reading at 275 nm from the reading at 220 nm to get the absorbance due to nitrate. Convert this absorbance value into equivalent nitrate by reading the nitrate value from a standard calibration curve obtained at 220 nm.

$$Nitrate\ (N;\ mg.L^{-1}) = \frac{Net\ nitrate\ nitrogen\ (mg)}{Volume\ of\ sample\ (mL)}$$

$$NO_3^-(mg.L^{-1}) = Nitrate\ nitrogen\ (mg.L^{-1}) \times 4.43$$

Determination of sulfate in groundwater sample: Sulfate occurs naturally in groundwater and some time in surface water sources. But water-soluble sulfate minerals including sodium, potassium, and magnesium sulfate are largely discharged into water bodies from paper mills, textile mills, tanneries, mines, and smelters. The determination of sulfate (SO_4^{2-}) content in the water has been carried out by the titration method. For the estimation of sulfate, the alkalinity and the TH of the water sample must be determined before (Guidelines for drinking water quality, 1997; Manual on water and wastewater analysis, PHED-Rajasthan, 1991).

- **Apparatus:** Beaker, Burette, Pipette, and Stove.
- **Reagents:** Standard barium chloride ($BaCl_2$), ammonia–ammonium buffer (NH_4Cl), Erichrome black–T indicator, and 0.01M standard Ethylene diamine tetra acetic acid (EDTA) solution.
- **Procedure:** The detailed procedures for estimation of SO_4^{2-} ion concentration from water sample considering the following steps:

(i) We take 100 mL of water sample followed by adding small amount of methyl orange indicator and a slight excess of HNO_3 followed by boiling the mixture to remove dissolved CO_2.

(ii) Now add 10 mL std. $BaCl_2$ solution in the boiling solution and then allow it to cool and make up the volume up to 150 mL.

(iii) We add 1.0 mL of buffer solution and small amount of Erichrome Black–T (EBT) indicator.

(iv) Now, titrate the solution with EDTA solution tillaneternal blue color. The blue colourspecifying the endpoint of the titration and calculate the sulfate content in water sample using the following formula:

$$\begin{matrix} Sulfate \\ (mg/L \end{matrix} = \left(\begin{matrix} Titrate\ value \\ in\ hardness \\ estimation \end{matrix} + \begin{matrix} Value\ equivalent \\ to\ volume\ of\ BaCl_2 \\ solution\ used \end{matrix} - \begin{matrix} Titrate\ value \\ in\ sulfate \\ determination \end{matrix} \right) \text{ x } 0.98 \text{ x } \frac{1000}{mL\ of\ sample}$$

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