Determination of Sodium and Potassium in groundwater

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Introduction
Determination of Sodium and Potassium in groundwater sample: Sodium (Na\(^+\)) and potassium (K\(^+\)) ions are naturally present in underground water and sometimes in surface water like salt-lake (Sambhar Salt Lake, Rajasthan). Both ions in water have been determined by the flame photometric method in the present study. This is centred on the emission spectroscopy, which contracts through the transfer of electrons from ground state to excited energy state and coming back to its original state with the emission of light.

➢ Principle: Sodium and Potassium dissociates into atoms when the sample solution sprayed on the flame with the help of an atomizer. Few of them become excited to higher energy levels, but not stable at higher energy levels. Thus, they emit radiations of specific wavelength when returning to the ground state. The emitted radiation generally belongs to the visible region. The intensity of emitted radiation can be measured by a photo-detector.

After prudently calibrating the flame photometer with a known concentration solution, it is likely to correlate the intensity of a given spectral line of the unknown water sample with the amount of an element that emits the particular radiation. The intensity of the emitted radiation is directly proportional to the concentration of the sample.

Below the emitted radiation wavelength and flame color for Na and K:

<table>
<thead>
<tr>
<th>Entry</th>
<th>Element name</th>
<th>Emitted radiation wavelength (nm)</th>
<th>Flame colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sodium (Na(^+))</td>
<td>589 nm</td>
<td>Yellow</td>
</tr>
<tr>
<td>2</td>
<td>Potassium (K(^+))</td>
<td>766 nm</td>
<td>Violet</td>
</tr>
</tbody>
</table>

➢ Apparatus: Flame photometer with flame accessories.

➢ Reagents: Distilled water; stock sodium solution (1 mg/mL Na\(^+\)), and stock potassium solution (1 mg/mL K\(^+\)).

➢ Procedure: The detailed procedures for measuring the Na\(^+\) and K\(^+\) ion concentration from water sample considering the following steps:

(i) We turned on the air-gas mixture and calibrated the flame by adjusting the air-gas mixture to obtain the blue flame. The flame was then allowed to stabilize for about 5 min.

(ii) Then, we switched on the remaining instrument and opened the lid of the filter chamber.

(iii) The galvanometer’s readings were adjusted to zero by spraying distilled water into the flame.

(iv) The sensitivity of the galvanometer reading to the desired mark was adjusted by spraying the most concentrated standard working solutions into the flame.

(v) Again, galvanometer’s readings were readjusted to zero by spraying distilled water into the flame.

(vi) Now, each of the standard stock solutions was sprayed thrice for each solution into the flame and recorded the galvanometer readings.

(vii) After each analysis, the instrument was carefully washed before starting new sample analysis.

(viii) The water sample was sprayed into the flame and recorded the galvanometer readings. This step was repeated thrice for each sample.

Finally, we plot the graph between concentrations and mean galvanometer reading to find out the element concentration in the unknown water sample.
1. **Determination of total hardness (TH; Ca & Mg) and Ca-hardness of groundwater sample:** Total hardness (TH) of water is generally comprising dissolved polyvalent metallic ions such as Ca and Mg. Some other polyvalent metallic ions also contribute in TH in minor quantities such as Al, Ba, Fe, Mn, Sr, Zn etc. The principal natural sources of hardness in water are sedimentary rocks, soil run-off, limestone etc. The TH of water has been determined by Titrimetric (Complexometric titration) method.

➢ **Principle:** In alkaline situation, EDTA reacts with Ca and Mg to produce a water-soluble chelated complex. Ca\(^{2+}\) and Mg\(^{2+}\) ions produce wine red color with EBT indicator under alkaline situation. Ca\(^{2+}\) and Mg\(^{2+}\) ions get complexed with EDTA and resulting in a color change from wine red to blue, which specifies the endpoint of the titration.

The pH for this titration has to be persistent at 10 ± 0.1. At higher pH, i.e., at about pH 12.0, Mg\(^{2+}\) ion precipitates and only Ca\(^{2+}\) ion remains in solution. At this pH, murexide (ammonium purpurate) indicator forms a pink color with Ca\(^{2+}\) ion. Ca\(^{2+}\) ion gets complexed with EDTA and resulting in a color change from pink to purple, which indicates the endpoint of the titration.

The detailed titration reactions of total harness and Ca-hardness are as follow:

**A. Total hardness (Ca & Mg):**

\[
[Ca^{2+}Mg^{2+}] + EBT \xrightarrow{pH \, 10} [EBT - Ca^{2+}Mg^{2+}] \text{chelate}
\]

Wine red \quad \text{Blue}

\[
[EBT - Ca^{2+}Mg^{2+}] + EDTA \rightarrow [EDTA - Ca^{2+}Mg^{2+}] \text{chelate} + EBT
\]

**B. Ca-hardness:**

\[
[Ca^{2+}] + \text{Murexide} \xrightarrow{pH>10} [\text{Murexide} - Ca^{2+}] \text{chelate}
\]

Pink \quad \text{Purple}

\[
[\text{Murexide} - Ca^{2+}] \text{chelate} + EDTA \rightarrow [EDTA - Ca^{2+}] \text{chelate} + \text{Murexide}
\]

➢ **Apparatus:** Burette, pipette, conical flask, measuring flask etc.

➢ **Reagents:** Eriochrome Black-T indicator, Murexide (ammonium purpurate) indicator, Standard EDTA solution (0.01M), Standard CaCO\(_3\) solution (1 mg/mL CaCO\(_3\)), Hydroxylamine hydrochloride (Inhibitor), Buffer solution, and Sodium hydroxide (NaOH; 2N).

➢ **Procedure:** The detailed procedure for measuring the TH, Ca- and Mg-hardness of water sample:

**A. Total hardness (TH):**

(i) We take 10 mL of water sample in a conical flask followed by adding 2 mL of buffer solution and 1mL of inhibitor and mix well before performing the titration.

(ii) Now add a pinch of EBT indicator and titrate against 0.01M standard EDTA till wine red color change to blue and record the reading of used EDTA.

(iii) We repeat the above titration with blank.

(iv) Finally, we calculate the TH in water sample using the following equations:

\[
\text{Total hardness as CaCO}_3 (mg/L) = \frac{(A - B) \times 1000}{\text{mL of sample}}
\]

Where, \(A = \text{EDTA required for sample (mL)}\); \(B = \text{EDTA required for blank (mL)}\).

**B. Ca-hardness:**
(i) Take 10 mL of water sample in a conical flask followed by adding 2 mL of NaOH solution and a pinch of Murexide indicator.

(ii) Titrate the solution against 0.01M standard EDTA till pink color change to purple and record the reading of used EDTA.

(iii) Repeat the above titration with blank.

(iv) Finally, calculate the TH in water sample using the following equations:

\[
\text{Calcium hardness as } CaCO_3 (mg/L) = \frac{(A - B) \times 1000}{mL \text{ of sample}}
\]

Where, A = EDTA required for sample (mL); B = EDTA required for blank (mL).

C. Mg-hardness: Mg-hardness can be calculated using the following equation:

\[
\text{Mg hardness (mg/L) = Total hardness } - \text{ Ca hardness}
\]

2. Determination of carbonate and bicarbonate in groundwater sample: The carbonate (CO\(_3^{2-}\)) and bicarbonate (HCO\(_3^-\)) ions are primarily originated from the dissolution of carbonate minerals in most natural surface water and underground water bodies. Carbonate (CO\(_3^{2-}\)) and bicarbonate (HCO\(_3^-\)) ions were determined by titrimetric method. In Titrimetric method, the titration of an identified volume of water samples against std. H\(_2\)SO\(_4\) using phenolphthalein and methyl orange indicators simultaneously.

- **Apparatus:** Conical flask, Pipette, Burette, Measuring flask etc.
- **Reagents:** Sulfuric acid solution (0.01N), methyl orange indicators, and phenolphthalein indicator.
- **Procedure:** The detailed procedure for estimation of CO\(_3^{2-}\) and HCO\(_3^-\) ions from water sample considering the following steps:

  (i) We take 10 mL sample in a 100mL conical flask and then add 2 drops of phenolphthalein indicator. The pink color of the solution shows the presence of carbonate ion in the solution.

  (ii) Now titrate the above solution against 0.01N sulfuric acid until the color change indicating the endpoint of the titration.

  (iii) Now add 2 drops of methyl orange indicator, yellow color was appeared and continue the titration with 0.01N sulfuric acid until the yellow color changes to red color.

  (iv) Calculate the CO\(_3^{2-}\) and HCO\(_3^-\) ions concentration in the water sample using the following formula:

\[
\text{CO}_3^{2-} (mg/L) = \frac{2 \times N \times A \times 1000 \times 30}{mL \text{ of sample}}
\]

\[
\text{HCO}_3^- (mg/L) = \frac{N \times (B - A) \times 1000 \times 61}{mL \text{ of sample}}
\]

Where, N = Normality of acid; A = Volume of titrant against phenolphthalein indicator (mL), and B = Volume of titrant against methyl orange indicator (mL).

III.4.1 Graphical and Statistical Analysis of Data: Graphical and statistical techniques were used to analyze the available water quality data of groundwater of Kathumar block of Alwar district (Rajasthan). Graphical analyses were used to graphical representation of the aerial distribution of dissolved constituents in water throughout the season and location, and to elucidate the typical chemical characters of the water samples. Statistical analyses indicate the valuable generalizations about the water sample quality of the location, such as the average concentration of a dissolved constituent and the expected variability. Quality of water is determined by chemical analysis and the obtained data are used for various purposes such as classification, analysis, correlation etc. For these purposes, the collected data need to be compiled and statistically evaluated. Based on graphical and statistical...
examination, the several dimension of refining water quality for human consumption, irrigation, and other domestic purposes have also been recommended.

### III.4.2 Evaluation of water quality index (WQI) for drinking purpose

WQI is defined as a technique of rating the water quality that delivers the overall water quality for human consumption.

A WQI mainly consists of an easier expression of more or less complex parameters, which serve as a water quality measurement. WQI indicating the drinking water quality in terms of index number and therefore, it offers a single number that indicates overall water quality at a definite locality and interval. Thus, WQI is asignificantpractice that defines both surface water and groundwater and its appropriateness for human beings consumption.

Adak and Purohit (2001) suggested a water quality indexing system for the purpose of the appropriateness of water for drinking purpose (Adak and Purohit, 2001). The WQI can be calculated from the following equation:

$$WQI = \text{Antilog}(\sum W_n \log Q_n)$$

Where: $W_n =$ Weight of the pollutants in the sample ($W_n = K/S_n$); $K =$ Constant [$K = 1/(1/S_1 + 1/S_2 + 1/S_3 + \ldots + 1/S_n)$]; $S_n =$ Standard values for different water quality parameters; $Q_n =$ Water Quality Rating [$Q_n = 100 x (V_n - V_1)/(S_n - V_1)$]; $V_n =$ Observed Values; $V_1 =$ Ideal Values ($V_1 = 7.0$ for pH and $V_1 = 0.0$ for all other parameters).

Note: WHO-2003 standard values were used in calculations for WQI and rating for WQI presented in Appendix–I. Alkalinity and all heavy metals (like Cr, Cu, Cd, Mn, Ni, Pb, Fe, As & Zn) have not been included in calculation for WQI.

### References: