Chloride

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Chloride

* Chloride, in the form of the Cl\(^-\) ion,
* one of the major inorganic anions in saltwater and freshwater.
* It originates from the dissociation of salts, such as sodium chloride or calcium chloride, in water.

\[
\text{NaCl(s)} \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)
\]

\[
\text{CaCl}_2(s) \rightarrow \text{Ca}^{2+}(aq) + 2 \text{Cl}^-(aq)
\]
**Chloride**

* Variable concentrations in natural water sources
  * Low \([\text{Cl}^-]\) → upland and mountain supplies
  * High \([\text{Cl}^-]\) → river and groundwaters
  * Very high \([\text{Cl}^-]\) → Sea and ocean waters
* As mineral content ↑ → chloride content ↑
Sources of Chloride

- Surface waters dissolve chlorides from top soil.
- Spray from the ocean is carried in land as droplets or flooding.
- Ocean and sea waters invade the rivers that drain into them.
- Intermixing between freshwater and saltwater layers
Salt water intrusion
How over-pumping can impact neighbours and streams
How saline water reaches the crops:

In arid regions, soil drainage is often poor, evaporation rates are high and the water table is low.

Poor drainage and evaporation concentrate salts on irrigated land. Even good quality irrigation water contains some dissolved salt and can leave behind tonnes of salt per hectare each year.

Unless salts are washed down below root level, soil salinity will stunt growth and eventually kill off all but the most resistant plants.

Irrigation can raise groundwater levels to within a metre of the surface, bringing up more dissolved salts from the aquifer, subsoil and root zone.
Chloride in wastewater

* Human urine contain chloride → originating from consumed food and water
  
  6 gr Cl⁻ / person / day

* This increases the amount of Cl⁻ in municipal wastewater about 15 mg/L

* Many industrial wastes contain high amounts of chloride
Significance of Chloride

* Not harmful to humans at reasonable concentrations
  * Conc. >250 mg/L → salty taste to water
* Secondary standard
  * EPA=250 mg/L
  * WHO=250 mg/L
  * Turkish standards=250 mg/L
* In regions where water is scarce, conc. as high as 2000 mg/L → people get used to it.
How are salts harmful to plants

- CAUTION: Salinity is not only due to Cl-, but also due to other ions like Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, SO$_4^{2-}$, HCO$_3^-$

- Osmotic influences
- Specific ion toxicity

(Adapted from Maas and Hoffman 1977).
**Turkish Standards on Irrigation water**

* Teknik Usuller Tebligi, 2010

### Table E7.2 Sulama suyunun kimyasal kalitesinin değerlendirilmesi için geliştirilmiş tablo

<table>
<thead>
<tr>
<th>Parametreler</th>
<th>Birimler</th>
<th>Kullanında zarar derecesi</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Yok (I. smif su)</td>
</tr>
<tr>
<td><strong>Tuzluluk</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>İletkenlik</td>
<td>μS/cm</td>
<td>&lt; 700</td>
</tr>
<tr>
<td>Toplam çözümnüş Madde</td>
<td>mg/L</td>
<td>&lt; 500</td>
</tr>
<tr>
<td><strong>Geçirgenlik</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SAR_{Tad}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0-3</td>
<td>EC</td>
<td>≥ 0.7</td>
</tr>
<tr>
<td>3-6</td>
<td></td>
<td>≥ 1.2</td>
</tr>
<tr>
<td>6-12</td>
<td></td>
<td>≥ 1.9</td>
</tr>
<tr>
<td>12-20</td>
<td></td>
<td>≥ 2.9</td>
</tr>
<tr>
<td>20-40</td>
<td></td>
<td>≥ 5.0</td>
</tr>
<tr>
<td><strong>Özgül iyon toksisitesi</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodyum (Na)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yüzey sulaması</td>
<td>mg/L</td>
<td>&lt; 3</td>
</tr>
<tr>
<td>Damlatmalı sulama</td>
<td>mg/L</td>
<td>&lt; 70</td>
</tr>
<tr>
<td>Klorür (Cl)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yüzey sulaması</td>
<td>mg/L</td>
<td>&lt; 140</td>
</tr>
<tr>
<td>Damlatmalı sulama</td>
<td>mg/L</td>
<td>&lt; 100</td>
</tr>
<tr>
<td>Bor (B)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mg/L</td>
<td>&lt; 0.7</td>
<td>0.7-3.0</td>
</tr>
</tbody>
</table>

### Specific ion toxicity

**Table E7.5 Bitkilerin yapraklarına zarar veren klorür konsantrasyonları**

<table>
<thead>
<tr>
<th>Hassaslık</th>
<th>Klorür konsantrasyonu, mg/L</th>
<th>Etkilenen bitki</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hassas</td>
<td>&lt; 178</td>
<td>Badem, kayısı, erik</td>
</tr>
<tr>
<td>Orta hassas</td>
<td>178-355</td>
<td>Üzüm, biber, patates, domates</td>
</tr>
<tr>
<td>Orta toleranslı</td>
<td>355-710</td>
<td>Kaba yonca, arpa, müsür, salatalık</td>
</tr>
<tr>
<td>Toleranslı</td>
<td>&gt; 710</td>
<td>Karnabahar, pamuk, susam, sorgum, şeker pancarı, ayçiçeği</td>
</tr>
</tbody>
</table>
Specific ion toxicity of Chloride on plants
**Heavily salted**

Salinity affects as much as one-quarter of the irrigated land in some countries:

<table>
<thead>
<tr>
<th>Country</th>
<th>Percentage salinated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mexico</td>
<td>10</td>
</tr>
<tr>
<td>India</td>
<td>11</td>
</tr>
<tr>
<td>Pakistan</td>
<td>21</td>
</tr>
<tr>
<td>China</td>
<td>23</td>
</tr>
<tr>
<td>United states</td>
<td>28</td>
</tr>
</tbody>
</table>
Methods of determination

* Argentometric Method
* Potentiometric procedure
  * Silver nitrate to form AgCl complex and employ a silver-silver chloride electrode system to detect the end point
* Mercuric Nitrate Method → reading assignment
* Ferricyanide Method
* Ion chromatography
Inside of the tube is a reference solution, which contains a known and fixed concentration of analyte (Cl\(^-\)) solution.

any change in measured potential is caused only by a change in potential across the membrane and is a function of the analyte chloride ion activity (or concentration).
Mohr (Argentometric) Method

* **Argentometry** is a type of titration involving the silver(I) ion
* Employs silver nitrate as the titrant
  
  $0.0141 \text{ N silver nitrate (N/71)}$ Each ml = 0.5 mg Cl$^-$
* Potassium chromate as the indicator
* Turns to reddish-brown at the endpoint

$$\text{Cl}^- \text{ (in mg/L)} = \frac{(\text{mL} \text{ AgNO}_3 - \text{blank}) \times 0.5 \times 1000}{\text{mL sample}}$$

Since $0.0141 \times 35.45 = 0.5$. 
Ex: \[ \text{Ag}^+ + \text{Cl}^- \rightleftharpoons \text{AgCl}_{\text{white}} \]

- At chemical equivalence:
  \[ [\text{Ag}^+] = \sqrt{K_{sp}} = \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5} \text{ M} \]

- And \[ 2 \text{Ag}^+ + \text{CrO}_4^{2-} \rightleftharpoons \text{Ag}_2\text{CrO}_4(s) \]

  \[ [\text{CrO}_4^{2-}] = \frac{K_{sp}}{[\text{Ag}^+]^2} = \frac{1.2 \times 10^{-12}}{(1.35 \times 10^{-5})^2} = 6.6 \times 10^{-3} \text{ M} \]
Mohr Method

1. A uniform sample size must be used, preferably 100 mL, so that ionic concentrations needed to indicate the end point will be constant.

2. The pH must be in the range of 7 to 8 because Ag⁺ is precipitated as AgOH(s) at high pH levels and the CrO₄²⁻ is converted to Cr₂O₇²⁻ at low pH levels.

3. A definite amount of indicator must be used to provide a certain concentration of CrO₄²⁻; otherwise Ag₂CrO₄(s) may form too soon or not soon enough.
100.0 mL of waste water is titrated using the Mohr method. A chromate endpoint is reached after addition of 16.43 mL of 0.09762 M AgNO₃. What is the chloride concentration in mg Cl⁻/L?
The Mohr titration has 1:1 stoichiometry

\[ M_1 V_1 = M_2 V_2 \]

\[ M_1 (100.0 \text{ mL}) = (0.09762 \text{ M})(16.43 \text{ mL}) \]

\[ M_1 = 0.01604 \text{ M Cl}^- \]

\[
0.01604 \text{ moles Cl}^- \times 35.453 \text{ g Cl}^- \times \frac{1000 \text{ mg}}{1 \text{ g}}
\]

\[ = 568.6 \text{ mg/L} \]

(which is actually pretty high – anything above 250 mg/L will taste salty)
Application of Chloride data

* Interferes with the measurement of COD
* Used as a tracer