

Analysis of chloride in water

We all know that seawater is salty. We also know that this is due, in the main, to the presence of sodium chloride. (To be more precise, there is not actual sodium chloride present, merely sodium ions and chloride ions along with a host of other anions and cations in smaller quantities but it is convenient to talk in terms of sodium chloride). There are also chloride ions in far smaller concentrations in many 'fresh' water sources. A glance at the compositions of mineral waters will show chloride as a significant component.

Salinity is important as many water dwelling organisms will only thrive within a particular salinity range and also, in agriculture, increasing salinity of soils has implications for loss of production.

The average concentration in seawater worldwide is 3.5% (usually given as 35 ppt - parts per thousand) but the figure will vary depending on a variety of factors.

Argentometry

The analysis of chloride is done by argentometry - titrating with silver salts.

Mohr's method

The most common method, familiar in schools, is Mohr's method.

This involved titration with silver nitrate solution using potassium chromate as an indicator.

As you slowly add silver nitrate solution, a white precipitate of silver chloride forms (although it is coloured yellow by the chromate ions).



The end point occurs when all the chloride ions are precipitated. Then additional silver ions react with the chromate ions of the indicator, potassium chromate, to form a red-brown precipitate of silver chromate.

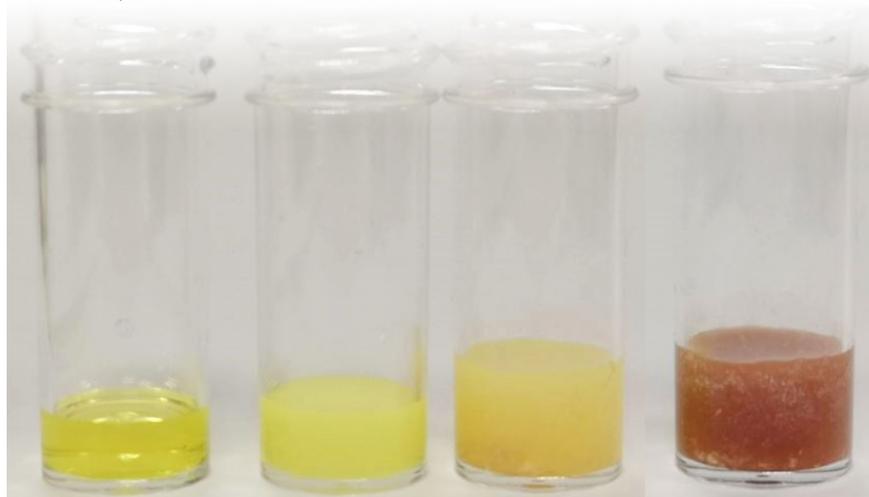
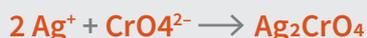


Figure 1 - Chromate. L-R Starting solution, silver chloride precipitate, end-point colour change, going further.

While this method works well, it has the problem of using chromate which is toxic and dangerous for the environment. But there are alternatives.

In both of these cases, the actual titration is carried out in exactly the same way as normal just using different indicators (and in the second one doing some preparation to the water sample).

Fajan's method

This alternative uses an adsorption indicator such as fluorescein. The indicator adsorbs onto the surface of the silver salt precipitate at the endpoint. This adsorption process causes a change in the colour of the indicator.

Common Fajan's adsorption indicators are weakly acidic organic compounds and in alkaline conditions will exist as the conjugate base, In-. It is this form of the indicator which interacts with the precipitate.

When AgNO_3 is added to a dilute solution of NaCl , the solution becomes turbid and coagulation does not usually occur immediately. The colloidal sized AgCl particles adsorb Cl^- and these attract sodium ions. Colloidal particles are electrically charged and repel each other preventing coagulation.

As titration continues, the amount of chloride decreases but there is still some surface charge which acts to repel the negatively charged indicator ion. Immediately after the endpoint there is an excess of silver ions which will adsorb onto the surface of the precipitate.

The charged surface has now changed polarity and attracts the negative indicator ion causing an observable colour change. >>

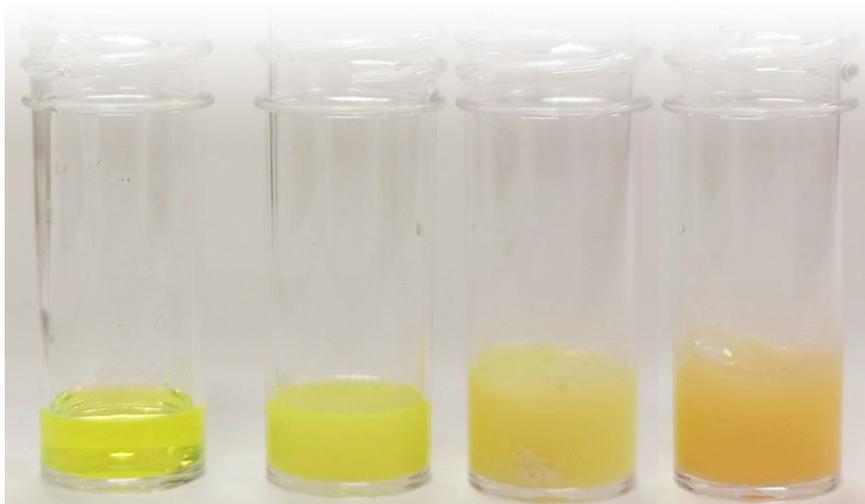


Figure 2 - Fluorescein. L-R Starting solution, silver chloride precipitate, end-point colour change, going further.

There is a variety of indicators that can be used. The most likely to be found in school are fluorescein and eosin. Fluorescein works from pH 7. Dichlorofluorescein is OK for more acidic solution (pH 4 and up) and eosin is fine above pH 1 BUT is unsuitable for chloride, though fine for bromide and iodide, as it binds too strongly.

There is, however, a new method.

The Hong-Kim-Czae method [1]

It utilizes a mediator, a weak acid that can form an insoluble salt with the titrant. The mediator triggers a sudden change in pH at an equivalence point in a titration. This change can then trigger a colour change in an indicator. The version here uses phenolphthalein [2] as an indicator but it does rely on mixing the sample with a phosphate solution to mediate the reaction.

A weak acid (HA) whose conjugate base (A^-) can form a slightly soluble salt (AgA) with the titrant (Ag^+) is added in place of the (chromate) above. The result is that at the equivalence point, H^+ ions are produced leading to a sharp drop in pH which allows the equivalence point to be detected with an acid-base indicator.

The water sample first has a small amount of phosphate added to it and then a few drops of sodium hydroxide to make it alkaline. This makes it purple when phenolphthalein is added.

At the equivalence point, the drop in pH turns the indicator from purple to a reddish brown (there is notable clumping shortly before the end). Theoretically, the end should be colourless but it seems not to be - the reasons are obscure at present - there is, however, a clear colour change.

Volhard's method is another alternative that is not discussed here due to cost factors.



Figure 3 - Phenolphthalein. L-R Starting solution, silver chloride precipitate, end-point colour change, going further.

It involves adding excess silver nitrate and then carrying out a back titration with an iron solution using thiocyanate as the indicator.

It is effective but has no real advantage over the previous methods and uses more silver nitrate.

Gravimetric method - this has also been discounted in this discussion as it needs significantly more silver nitrate to get an accurate result and there are also problems with the co-precipitation of other silver compounds such as sulphates.

In conclusion

Silver nitrate, like all silver compounds, is expensive. In order to minimise cost, where possible it is a good idea to use microscale titrations as they will use a small fraction of the amount that a full-scale titration will.

The lack of chromate contamination in these methods, though, will mean that of recycling the silver, while not simple, is more likely to be possible. We will follow this up in a future article. <<

References

- [1] The method has no name but these are the names of the authors of the paper.
- [2] <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3065052/pdf/IJAC2010-602939.pdf>.