Fundamentals of Analytical Chemistry, CHC014011L

Exercise 6:
Determination of Hardness of Water

Introduction:
Hardness in water is generally caused by the presence of dissolved calcium and magnesium carbonates and sulphates. The cations of these salts react with soap, regarding it insoluble and ineffective as a detergent. The hydrogen carbonates that cause hardness are decomposed on boiling according to the following equation:
$M(HCO_3)_2\,(aq) \rightarrow MCO_3\,(s) + H_2O + CO_2\,(g)$
where M = Ca or Mg
Hardness that is removed by this process is referred to as temporary hardness while that which remains after boiling is called permanent hardness. EDTA reacts quantitatively with both calcium and magnesium ions in a 1:1 stoichiometric ratio. It may be used to determination of water hardness.

Equations:
Titration: $Ca^{2+} + H_2Y^{2-} \rightarrow CaY^{2-} + 2\,H^+$
$Mg^{2+} + H_2Y^{2-} \rightarrow MgY^{2-} + 2\,H^+$
End point: $Mg^{2+} + HIn^{2-} \rightarrow MgIn^- + H^+$
$MgIn^- + H_2Y^{2-} \rightarrow MgY^{2-} + HIn^{2-} + H^+$
(red) (colourless) $\rightarrow$ (colourless) (blue)

Procedure:
Laboratory glassware has to be perfectly clean before it can be used for any type of analytical work.
Transfer by pipette 50.00 cm^3 (2 x 25.00 cm^3) of the water sample provided into a 250 cm^3 conical flask. Add to this 50 cm^3 distilled water, 1 cm^3 of 1% hydroxylamine and 1 cm^3 of 5% Na_2S solution. Introduce 1 cm^3 of buffer solution and 5 drops of Eriochrome Black T.
Titrate with standard Na_2H_2Y to a colour change from wine red through purple to a pure blue. Write down the volume of EDTA used. Repeat to obtain consistent titre values (min. three times).
Repeat the procedure for the tap water.

Calculate and report the hardness of waters (given and tap) as milligrams of $CaCO_3$ per litre.

Expression of results:

molarity of EDTA [mol/dm^3]:

titration no.	initial burette reading [cm^3]	final burette reading [cm^3]	titration [cm^3]
titration with the given water sample			

titration with the tap water			

Calculations:
given water
mean titration (volume of EDTA) [cm^3]:
hardness:

tap water
mean titration (volume of EDTA) [cm^3]:
hardness:

Exercise 7:
Determination of Chloride Ions by the Mohr method

Equations:

$$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$$
$$K_2CrO_4 + 2AgNO_3 \rightarrow Ag_2CrO_4\downarrow + 2KNO_3$$

Titrant: $AgNO_3$
Procedure:
Caution: any unused silver nitrate solution and the products of the titrations should be poured into the appropriate waste container.

Transfer (using pipette) 50.00 cm^3 of the given water sample into 250 cm^3 Erlenmeyer flask and dilute by adding 50 cm^3 of distilled water. Add 1 cm^3 of 10% potassium chromate (K_2CrO_4) to the flask. Rinse and fill a burette with the standard $AgNO_3$ solution. Titrate the water sample by adding the $AgNO_3$ solution slowly while mixing the sample. The end point will be indicated by the persistence of a red-brown colour through the yellow solution for about 30 seconds. Repeat the titration two more times and average the amount of $AgNO_3$ used to reach the endpoint.

Then titrate a blank using the same procedure above. For the blank use distilled water in place of the given water sample. The blank correction for the indicator should be subtracted from the average volume of the titrant obtained after titrating the given sample solution Subtract the volume of $AgNO_3$ for the blank from the used for the sample.
Repeat the procedure for the tap water.
Calculate and report the milligrams of iron in each portion of the unknown analysed along with the mean and the precision.

Expression of results:

molarity of $AgNO_3$ [mol/dm^3]:

titration no.	initial burette reading [cm^3]	final burette reading [cm^3]	titration [cm^3]
titration with the sample water			
titration with the blank solution			
titration with the tap water			

Calculations:
mean titration for the blank solution (volume of $AgNO_3$) [cm^3]:

given water
mean titration (volume of $AgNO_3$) [cm^3]:
concentration of chloride ions [mg/dm^3]:

tap water
mean titration (volume of $AgNO_3$) [cm^3]:
concentration of chloride ions [mg/dm^3]:

Exercise 8:
Determination of Dissolved Oxygen in Water (Winkler's method)

Equations:

$$Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2 \downarrow \quad \text{(white precipitate)}$$
$$2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2 \downarrow \quad \text{(brown precipitate)}$$
$$MnO(OH)_2 + 2I^- + 4H^+ \rightarrow Mn^{2+} + I_2 + 3H_2O$$
$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Titrant: $Na_2S_2O_3$

Procedure:

The water sample is delivered in the bottle, in which it should be treated.
Remove bottle stopper and add 1 cm^3 of the manganous sulfate solution by inserting the pipette just below the surface of the liquid. Add 2 cm^3 of the alkaline potassium iodide (KI) solution under the surface of the liquid. Replace the stopper, avoid trapping air bubbles and shake well by inverting the bottle several times. Leave the bottle in a cool, dark place for at list 1 hour. Next, add 2 cm^3 of concentrated sulfuric acid by allowing the acid to run down the neck of the bottle above the surface of the liquid. Carefully stopper and invert several times to dissolve the floc.
Transfer 100.00 cm^3 of sample from the bottle into an Erlenmeyer flask. Titrate with sodium thiosulfate solution until the solution is a pale yellow (straw) colour. Record the amount of titrant used. Add a small quantity of starch indicator and titrate with sodium thiosulfate solution to the first disappearance of the blue colour. Record the total number of cm^3 of sodium thiosulfate used.
Calculate and report the concentration of dissolved oxygen in your unknown sample.

Expression of results:

molarity of $Na_2S_2O_3$ (in mol/dm^3):

titration no.	initial burette reading [cm^3]	final burette reading [cm^3]	titration [cm^3]

Calculations:
mean titration [cm^3]:
number of $Na_2S_2O_3$ moles:
number of O_2 moles:
concentration of dissolved oxygen [mg/dm^3]:

Exercise 9:
Spectrophotometric determination of ammoniacal nitrogen in water

Make up to the graduation mark the obtained solution in the 200.0 cm^3 volumetric flask with distilled water (until the bottom of the meniscus is just in line with the graduation mark on the neck of the flask - use a dropping pipette for this), stopper the flask firmly and mix the solution by inverting the flask at least 10 times.

Preparing Calibration Curve
Standards must be treated in the same manner as samples.
Prepare standard solutions by pipetting of 0 µl, 100 µl, 200 µl, 300 µl, 400 µl, 500 µl, 600 µl, 700 µl, 800 µl of standard solution of ammonium chloride (100 ppm) into the 50 cm^3 volumetric flasks, add approximately 25 cm^3 of ammonia free distilled water and swirl gently. Next, add 0.5 cm^3 of sodium potassium tartrate tetrahydrate solution ($NaKC_4H_4O_6 \cdot 4H_2O$, masking agent) and 0.5 cm^3 of Nessler reagent (0.09 mol/L solution of potassium tetraiodomercurate(II), $K_2[HgI_4]$, in 2.5 mol/L potassium hydroxide), mix and dilute to 50.00 cm^3 with ammonia free water.
Allow 10 minutes for colour development.
Remember: sample, blank, and standards must be maintained at the same temperature and colour development time.
Read and record the absorbance of each mixture at 420 nm. (It is usually not necessary to check the blank before each measurement, but the instrument may drift, so it is wise to check the blank occasionally and readjust it to read 0 % Absorbance.)
Plot the absorbance of the standards readings at 420 nm (on the Y-axis) versus the micrograms of nitrogen in the standard (on the X-axis) on standard graph paper (use of the Excel program is allowed) to make a calibration curve. If the solutions follow Beer's Law, the data will fall on a straight line. This standard curve can be then use to determine the ammoniacal nitrogen concentration in the given sample. Determine the slope and y-intercept of the calibration curve and use them for calculation of the ammoniacal nitrogen concentration in the given solution.

Sample preparation procedure
Remove a 25.00 cm^3 aliquot of the given sample with a 25-mL volumetric pipet and transfer it to a clean and labelled 50 cm^3 volumetric flask. Add about 10 cm^3 of ammonia free distilled water and swirl gently. Then add 0.5 cm^3 of sodium potassium tartrate tetrahydrate solution and 0.5 cm3 of Nessler reagent. Dilute to the mark with ammonia free distilled water and mix thoroughly. Let this solution stand for at least 10 minutes before measuring the absorbance.
Warning: You need to make "blank" solution containing sodium potassium tartrate tetrahydrate solution, Nessler reagent and ammonia free distilled water to "re-zero" the spectrophotometer before measuring the absorbance of the sample solutions.

Calculate the ammoniacal nitrogen content in the original (given) water solution.

Expression of results:

Absorbance readings:

sample or standard no.	ammoniacal nitrogen concentration [mg/dm^3]	absorbance [A

Calculations:
calibration curve slope:
calibration curve slope:
concentration of ammoniacal nitrogen in the 50 cm^3 volumetric flask [mg/dm^3]:
content of dissolved oxygen in the given solution [mg]:

Write up a report for the exercises. Your report should include:

a. the underlying chemical principle of your method,
b. procedures,
c. tables summarizing titration results,
d. treatment of data involving calculations,
e. a conclusion of the investigation and
f. comment on the results obtained.

Tasks for pre-lab quiz:
argentometric titrations
precipitation titration; argentometry; titrimetric analysis of chloride; Mohr method and Volhard method - general remarks, reactions, end point detection, solutions used, procedure, result calculation, sources of errors

water hardness
definition; determination of the total hardness of water - general remarks, reactions, end point detection, solutions used, procedure, result calculation, sources of errors; complexometric titration; determination of calcium in presence of magnesium; determination of magnesium; calculations

dissolved oxygen
determination of dissolved oxygen; the Winkler method - general remarks, reactions, end point detection, solutions used, procedure, result calculation, sources of errors

spectrophotometry
principles of spectrophotometry; Beer-Lambert's Law; different types of spectrophotometers; spectrophotometric analysis - experimental procedure, preparation of calibration curves; determination of ammoniacal nitrogen - general remarks, reactions, solutions used, procedure, result calculation, sources of errors.

http://www.zcha.pwr.wroc.pl/dydaktyka/Fundamentals of analytical chemistry