DETERMINATION OF ULTRA LOW CHLORIDE SAMPLES

Chloride is indirectly measured in this method by using a silver ISE and a sample subtraction method. The silver ISE has a much lower limit of detection than the chloride ISE, so this method allows for the determination of trace chloride. This method utilises the 1:1 reaction between silver ions and chloride ions to form insoluble silver chloride in the reaction shown below.

$$Ag^+ + Cl^- \rightarrow AgCl_{(s)}$$

By measuring the corresponding decrease in silver ion concentration after the sample addition, we can determine the chloride concentration to a much lower concentration than that possible with the chloride ISE. The sample subtraction method can also allow for the determination of ions for species which themselves do not have a viable ISE.

Ensure that all beakers and volumetric flasks are rinsed thoroughly with deionised water and do not touch the inside of the beakers with bare hands as chloride contamination from sweat etc. is common, as is chloride contamination from tap water.

The use of an ISAB in this method is necessary due to minor variations in sample and standard ionic strength which will alter ion activity coefficients. Using a small amount of an ISAB that raises the overall ionic strength of each standard and solution to a point so high that these minor variations will be insignificant.

Equipment and Reagents Required

1. Ion meter, pH/mV analyser, or pH meter with millivolt scale
2. Silver combination ion selective electrode
3. Silver 1000ppm standard solution
4. Potassium nitrate ISAB solution (1M)
5. Glassware: 250ml beakers,100ml volumetric flask, 250ml volumetric flask, graduated pipette
6. Deionised water

Standard Preparation

Prepare standards of 1 and 0.1ppm by serial dilution of the 1000ppm standard solution. This is best achieved by pipetting 10ml of the standard into a 100ml volumetric flask and diluting to the mark with deionised water. This is now a 100ppm standard, repeat this step using the freshly made 100ppm standard to make 10ppm and so on until the desired concentration is reached. Store in a clean and sealed glass bottle. These low strength standards will contaminate very easily so it is best to make fresh daily. If the expected response is less than 0.1ppm chloride, then a further serial dilution step can be done to give 0.1ppm and 0.01ppm standards instead. – Note this is reaching the lower limit of detection, so at this concentration the ideal slope of the sensor (~59mV at 25°C) may not be reached.

Method

Pour 100ml of each of the standards and samples into clean and DI rinsed beakers and add 2ml of ISAB to each standard and sample.

Immerse the electrode in each of the standards in increasing concentration ensuring to rinse the electrodes with deionised water and dabbing off the excess water between standards. Record the mV

response in each standard and plot a graph of mV vs. log of concentration and determine the slope of the calibration curve or follow the calibration routine on the ion meter, if available.

Now that the calibration curve for silver has been determined add 10ml of your unknown chloride solution to your 1ppm standard (mV1) and stir using the probe for 15 seconds to ensure homogeneity and to allow all the chloride to react and precipitate out of solution. Let the probe settle and record the response (mV2). Some ion meters will have a sample subtraction method included in the software, if this is not the case use the following calculation.

Calculation

The following equation can be used to calculate the amount of chloride present in the sample:

$$C_u = C_s \left[\frac{V_u + V_s}{V_u}\right]\left[10^{\frac{\Delta E}{S}} - \frac{V_s}{V_s + V_u}\right]$$

Variables

Cu = Concentration of unknown sample (mol/L)

Cs = Concentration of known sample (mol/L)

Vu = Volume of unknown sample (L)

Vs = Volume of known sample (L)

S= Probe slope(mV) - (determined from the calibration stage)

ΔE = Change in probe potential (mV1-mV2)